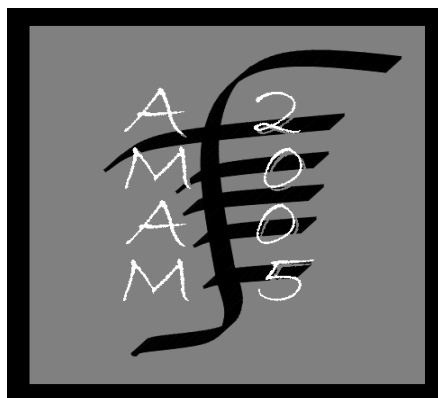


International Conference on

ASBESTOS MONITORING AND ANALYTICAL METHODS

- AMAM 2005 -



Scientific Committee

M. Alessi	Health Ministry
G. Cecchetti	Urbino University
S. Clarelli	ASSOAMIANTO
G. Clerici	Turin University
J. Dyczek	Krakow University
M. Giangrasso	Environmental Ministry
L. Kazan Allen	IBAS-UK
E. Lauria	ARPA Piemonte
G. Ludovisi	ISPESL
A. Marabini	CNR
A. Marconi	ISS
L. Musmeci	ISS
F. Paglietti	ISPESL
M. Palumbo	CNR
L. Paoletti	ISS
S. Polizzi (Chair)	Venice University
E. Renna	ARPA Emilia Romagna
A. Verardo	Regione Liguria
M. Wojtowicz	ARPA-Piemonte

Organizing Committee

F. Agnoli	Venice University
L. Bertoldo	Venice University
F. Cappa	ISPESL
F. Damiani	ISPESL
T. Finotto	Venice University
S. Malinconico	ISPESL
L. Zamengo	Venice University

Organizing Secretariat

ASSOAMIANTO - IBAQ SLR
ISTITUTO PER LA QUALITA' DELLA
BONIFICA AMIANTO-AMBIENTE

Presentazione

Questo congresso nasce come attività di divulgazione del progetto europeo LIFE-Ambiente denominato FALL, iniziato nell'ottobre 2003 e volto ad affrontare il problema del possibile rischio rappresentato dai percolati delle discariche contenenti amianto (vedi Abstract a pg.45). La valutazione del rischio presuppone l'esistenza di metodi analitici adeguati e la presenza di norme di legge che stabiliscano limiti chiari e prescrivano i protocolli di misura. Nel caso dei percolati di discarica né l'una, né l'altra di queste condizioni sono rispettate in Italia, situazione che è il probabile risultato di una scarsa attenzione al problema da parte della comunità scientifica. Da questo è nata la duplice esigenza di portare l'attenzione degli operatori del settore su questa problematica e di confrontare le diverse situazioni presenti negli altri paesi europei. Il congresso non si limiterà alla matrice liquida, ma avrà raggiunto il suo scopo se sarà riuscito a stimolare la sensibilità degli esperti riuniti a Venezia nei confronti di questo problema, partendo dalle conoscenze già acquisite in matrici come l'aria ed i solidi, dove le metodologie hanno ormai raggiunto un livello più consolidato.

La prima mezza giornata del congresso si propone di fare un breve quadro della situazione normativa europea. Nelle sessioni successive verranno discusse in sequenza le metodologie applicate per le tre matrici aria, solido e liquido. Seguirà la presentazione di lavori che affrontano le tematiche del monitoraggio e della mappatura ed infine una sessione sull'applicazione di metodi biologici per la determinazione per via indiretta della presenza di fibre pericolose nell'ambiente. Nella sessione poster verranno presentati alcuni interessanti lavori che non hanno trovato spazio nel programma.

Ringrazio tutti coloro che hanno contribuito alla realizzazione del congresso: in primis la Dr.ssa Federica Paglietti, anima del progetto FALL e di questo convegno, il Comitato Scientifico tutto, il Comitato Locale, l'ISPESL e il Centro Scansetti. Esprimo inoltre riconoscenza all'Ing. Sergio Clarelli e Assoamianto per il sostegno organizzativo. Ringrazio inoltre la Provincia di Venezia e la Regione Veneto che hanno concesso il loro patrocinio.

Porgo ai partecipanti un caloroso benvenuto a Venezia e auguro a tutti un buon lavoro.



Stefano Polizzi
Chair of AMAM2005

Presentation

The present Conference belongs to the dissemination activities of the European LIFE-Environment project named FALL, which started on October 2003. The project aims at tackling the problem of the possible risks connected with the leachate of asbestos containing landfills (see Abstract on page.45). The possibility of assessing risks implies the existence of appropriate analytical methods along with the presence of regulations setting exposure limits and prescribing measurement protocols. In the case of landfill leachates none of these two conditions are met in Italy, probably due to a lack of awareness of the scientific community. From this circumstances a twofold need arose: drawing the attention of the scientific community to this topic, and comparing the Italian situation with other European countries. The Conference is not restricted to liquids, but its goal will be reached if it will be able to awaken the experts gathered in Venice to this problem, starting from the knowledge settled for air and bulk materials, where methodologies are well-established.

The first half-day of the Conference will give a brief survey on the state of the art of regulations in Europe. During the following three sessions analytical methods for air, bulk materials and liquids will be discussed one after the other. Later on, papers dealing with problems encountered in monitoring and mapping of asbestos will be presented. The last session will be dedicated to the application of biological methods to the indirect determination of the presence of dangerous fibres in the environment. Some interesting papers not included in the program for lack of time will be presented as posters.

I wish to thank all the people who contributed to the realisation this conference: first of all Dr. Federica Paglietti, the soul of the FALL project and of this Conference, the whole Scientific Committee, the Local Committee, ISPESL and Centro Scansetti. The organisational contribution of Ing. Sergio Clarelli and Assoamianto is greatly acknowledged. Last but not least, I wish to thank Provincia di Venezia and Regione Veneto for giving their patronage.

I welcome all participants in Venice and wish them a profitable work.



Stefano Polizzi
Chair of AMAM2005

Opening Session

L. Kazan-Allen	Global impact of Asbestos
J. Cherrie	Exposure limits in different countries
S. Clarelli	How to work with asbestos safety
F. Damiani	Italian Asbestos laws
M. Alessi	Italian National Asbestos Commission and its workgroups

GLOBAL IMPACT OF ASBESTOS

Laurie Kazan-Allen

International Ban Asbestos Secretariat (IBAS), UK

Between the beginning of the 20th century and the 1940s, world production of asbestos rose by 2000%. Output grew steadily, peaking in 1975 at 5 million tons. Despite a slight downturn, annual production remained at over 4 million tons until 1991. In 2004, 2.2 million tons of asbestos were mined. Dr. Jukka Takala, Director of InFocus Programme SafeWork at the International Labour Office, estimated that there were 100,000 work-related asbestos deaths worldwide every year; he wrote:

“The global figure is growing as more people will die from (asbestos) cancer as communicable diseases are reduced... reductions (in asbestos-related deaths) will take place maybe only after 2020 if China and India introduce quickly measures against asbestos.”

Dr. Takala's figure of 100,000 deaths is often quoted in articles about asbestos. Unfortunately, what many people fail to appreciate is that this figure only relates to occupational asbestos exposure. Studies undertaken in South Africa, the UK, Italy, Spain, Poland and Canada detail the impact of environmental asbestos exposures on local populations. Unfortunately, this source of contamination has produced and continues to produce many asbestos victims. Professor Joe LaDou, who has studied the global migration of hazardous industries for a number of years, believes that:

“The asbestos cancer epidemic may take as many as 10 million lives before asbestos is banned worldwide and exposure is brought to an end... The battle against asbestos is in danger of being lost where the human cost may be the greatest, in developing countries desperate for industry.”

The paper which is being presented by Laurie Kazan-Allen at the conference: Asbestos Monitoring and Analytical Methods will look at incidences of environmental asbestos exposures experienced by communities in producing countries, consuming countries as well as hazardous asbestos contamination liberated during natural and man-made disasters. More specifically, the subjects which will be the focus of this paper include the impact of hazardous environmental exposures occurring in:

Producing Countries:

- the asbestos mining region of Thetford, Canada;
- Brazilian mining communities;
- Kazakhstan.

Consuming Countries:

- Spodden Valley, Rochdale, England where moves are being made to redevelop the 72 acre site of Turner & Newall's former asbestos textile factory;
- Amagasaki, Hyogo Prefecture, Japan;
- the Szczucin Community, Poland.

Disasters:

- the Great Hanshin-Awaji Earthquake 1995;
- the attack on the World Trade Centre 2001.

EXPOSURE LIMITS IN DIFFERENT COUNTRIES

J.W. Cherrie

Institute of Occupational Medicine, Research Park North, Edinburgh EH14 4AP, UK

Exposure limits are an important tool for the management of risks to health from hazardous substances. They must be protective of health, but may also reflect national socioeconomic conditions and administrative arrangements. In addition, countries may specify other secondary limit values, such as the concentration of asbestos permitted in ordinary waste material, that are used to manage situations where exposure could occur. There are therefore many potential differences from one country to another. This paper sets out a logical structure for asbestos limits, firstly to protect health and secondly as a means of managing situations where exposure might occur, and summarizes relevant limits in different countries.

There is clear scientific evidence that there are different levels of risk to health from different varieties of asbestos. For example, the risks of mesothelioma from inhalation of asbestos are greater for amphibole asbestos than for chrysotile. Therefore, current Occupational Exposure Limits (OEL) in many countries are lower for amphiboles (e.g. 0.2 fibres/ml in

the UK) than for chrysotile (0.3 fibres/ml in UK). However, under the new Asbestos Worker Protection Directive, the OEL will be reduced to 0.1 fibres/ml for all asbestos types. That reflects a judgement that tighter control is possible, although there is still an understanding of the relative risks with crocidolite more hazardous than amosite and both more dangerous than chrysotile.

The primary health concern from asbestos has always been inhalation of airborne fibres, particularly in workplaces. Most countries have OELs for asbestos, generally over an 8-hour working day, but in some cases over a shorter duration (e.g. 4 hours). There are also short duration exposure limits in some countries, to enable effective regulation of short-term tasks lasting for minutes rather than hours.

Limits for the air concentration of asbestos in other indoor situations are less common, but there are some limits for airborne fibre levels inside buildings when no active asbestos-related work is taking place. Some countries set limits for the acceptable fibre concentration in air after asbestos removal or remedial work is complete, sometimes called "clearance" levels. The analytical methods used for such samples also vary between countries, and these differences can substantially affect the measurements.

Levels of airborne asbestos in outdoor air are generally very low and few countries have felt it necessary to develop limits for such situations. However, there are some circumstances where risks from inhaling airborne fibres from environmental contamination occur and it may be necessary to have such limits.

There is some recent evidence that ingestion of high levels of asbestos in drinking water are associated with an increased stomach cancer risk; however there have also been negative studies showing no detectable effect from ingested asbestos contamination in water. Limits for asbestos in water may therefore be important to protect the health of people from the risks of consuming asbestos-contaminated water. Limits for asbestos in groundwater are also important for monitoring and managing the dispersal of asbestos fibres in water away from contaminated solid waste or environmental contamination.

Asbestos contamination in soil and solid waste does not present an important health risk until the fibres are dispersed into the air. One of the main issues is defining whether the fibres are available for being dispersed. Some limits are defined in terms of concentrations of friable materials or of non-friable materials containing asbestos. There is evidence that very low levels of contamination might present a risk to health if the soil is disturbed, if the asbestos is finely dispersed within the soil. Limits for asbestos in soil are very useful for managing asbestos contamination in the environment, but they may not be directly or easily related to risks to health. However, application of such limits may help prevent risks to health.

Finally, the situation for asbestos contamination in settled indoor dust is analogous to that of soil contamination. Limits for asbestos in such situations may be helpful in managing risks to health from contamination that has transferred inside houses or public buildings.

Data from a number of countries are compared and suggestions are made for a consistent set of limit values that are pragmatic and protect public health.

HOW TO WORK WITH ASBESTOS SAFETY

S. Clarelli

Presidente assoamianto www.assoamianto.it

Associazione tra consulenti, operatori nell'ambito della rimozione, smaltimento e bonifica dell'amianto e quanti sensibili alle problematiche ambientali inerenti

Le premesse indispensabili per lavorare in sicurezza con l'amianto sono:

- la qualificazione dell'impresa di bonifica;
- la protezione e l'abilitazione dei lavoratori e dei coordinatori dirigenti preposti alla bonifica;
- la protezione delle persone non interessate alle operazioni di bonifica;
- la protezione dell'ambiente circostante.

Un fondamentale elemento di garanzia di sicurezza è l'iscrizione dell'impresa di bonifica da amianto ad un albo specialistico (in Italia sussiste dal 2004 l'obbligo di iscrizione alla categoria 10 dell'Albo Gestori Rifiuti).

Per quanto riguarda la protezione dei lavoratori nelle operazioni di bonifica da amianto, essi, in primis, devono essere istruiti e informati, nonché abilitati:

- sulle tecniche di rimozione dell'amianto, con programma di addestramento all'uso delle maschere respiratorie;
- sulle procedure per la rimozione, la decontaminazione e la pulizia del luogo di lavoro.

Gli operai devono essere poi equipaggiati con adatti dispositivi di protezione individuali, vale a dire con maschere respiratorie, indumenti protettivi completi (tuta e copricapo), copriscarpe. Gli indumenti protettivi devono essere:

- di carta o tela plastificata a perdere (tyvek); in tal caso sono da trattare come rifiuti contaminati e quindi da smaltire come i materiali di risulta provenienti dalle operazioni di bonifica;
- di cotone o altro tessuto a tessitura compatta (da pulire a fine turno con accurata aspirazione, porre in contenitori

chiusi e lavare dopo ogni turno a cura della impresa o in lavanderia attrezzata);

Fondamentale è anche la figura del Coordinatore amianto, anch'egli abilitato, il quale dirige le operazioni di bonifica ed è tenuto a gestire le eventuali situazioni di emergenza.

Molto spesso al rischio biologico amianto è associato anche il rischio di caduta dall'alto, come nel caso della bonifica di coperture in cemento amianto, per cui è necessario adottare idonee opere provvisorie e qualsiasi necessario mezzo di protezione contro le cadute (individuale o collettivo). E' poi indispensabile seguire tutte le indicazioni previste nel Piano di lavoro, ex articolo 34 del D. Lgs. n. 277/91, che deve essere regolarmente approvato dal Servizio di prevenzione e sicurezza degli ambienti di lavoro dell'ASL competente per territorio. In ultimo, la Direttiva europea 2003/18/CE sulla protezione dei lavoratori contro i rischi connessi con l'esposizione all'amianto durante il lavoro (in Italia sta per essere pubblicato il relativo decreto legislativo di recepimento) prevede, tra l'altro, ulteriori misure per la protezione quali:

- l'abbassamento del valore limite di esposizione dei lavoratori a 0,1 fibre/cm cubo per qualsiasi tipologia di amianto;.
- l'istituzione di periodi di riposo per i lavoratori con dispositivo di protezione individuale delle vie respiratorie;
- l'accertamento dell'eventuale presenza di amianto prima di iniziare lavori di demolizione o di manutenzione.

ITALIAN ASBESTOS LAWS

F. Damiani, S. Malinconico, F. Paglietti

ISPESL, Istituto Superiore per la Prevenzione e la Sicurezza sul Lavoro, Roma, Italy

Il presente lavoro intende fornire un quadro sintetico del percorso normativo in materia di amianto.

Sono state prese in considerazione le principali norme e per ciascuna di esse sono state estratte le argomentazioni più rilevanti per le quali sono stati evidenziati gli sviluppi temporali.

Il primo strumento normativo di una certa rilevanza che affronta il problema amianto è costituito dal **D.P.R. 24 Maggio 1988, n. 215** emanato ai sensi dell'art. 15 della **Legge 16 Aprile 1987 n. 183**, in attuazione delle Direttive 83/478/CEE, 85/610/CEE relative alle restrizioni in materia di immissione sul mercato e di uso di talune sostanze e preparati pericolosi.

Con questo decreto veniva in sostanza vietata l'immissione sul mercato e la commercializzazione della crocidolite e dei prodotti correlati oltre all'obbligo dell'etichettatura dei prodotti contenenti alcune specificate fibre di amianto.

Tuttavia, è a partire dal **Decreto Legislativo del 15 Agosto 1991, n. 277**, emanato in attuazione delle direttive 80/1107/CEE, 82/605/CEE, 83/477/CEE, 86/188/CEE e n. 88/642/CEE in materia di regolamentazione dei rischi derivanti da esposizione ad agenti chimici fisici e biologici, che vengono affrontate per la prima volta le problematiche connesse alla protezione dei lavoratori contro i rischi da esposizione alla polvere proveniente dall'amianto o dai materiali contenenti amianto (MCA) durante le attività lavorative.

In esso viene anche introdotto l'obbligo, per il datore di lavoro, di provvedere ad una valutazione del rischio al fine di stabilire le misure preventive e protettive più idonee da attuare.

Si tratta, in particolare, di accertare l'inquinamento ambientale prodotto dalla polvere proveniente dall'amianto o dai materiali che lo contengono, di individuare i punti di emissione ed i punti a maggior rischio delle aree lavorative e di determinare l'esposizione personale dei lavoratori alla polvere di amianto.

Sono indicati anche i valori di soglia dell'esposizione (dosi-periodo di esposizione), le misure di prevenzione e protezione tecniche, organizzative, procedurali ed igieniche e stabiliti i controlli sanitari e le procedure di registrazione dei casi di asbestosi e mesotelioma asbesto-correlati.

La successiva **Legge 27 Marzo 1992 n. 257** riveste particolare rilievo in quanto stabilisce la cessazione dell'impiego dell'amianto, ed in particolare il divieto di estrazione, importazione, esportazione, commercializzazione e produzione di amianto, di prodotti di amianto e di prodotti contenenti amianto.

Inoltre, fissa e modifica alcuni valori limite indicati dal decreto 277 citato per gli ambienti lavorativi, introduce alcuni articoli per la tutela dell'ambiente e la salute (classificazione, imballaggio, etichettatura, controllo delle dispersioni durante le lavorazioni, rimozione dell'amianto e piani regionali e delle province autonome) e introduce misure di sostegno per i lavoratori ed alle imprese.

Proprio in applicazione delle misure di tutela ambientale introdotte dalla Legge 257 relative all'adozione dei Piani regionali e delle province autonome, il successivo **D.P.R. 8 Agosto 1994** stabilisce la predisposizione da parte delle Regioni e Province autonome di un censimento puntuale dell'amianto sul territorio di propria competenza e un conseguente piano di bonifica e gestione dei rifiuti.

Nello sviluppo, invece, delle normative e delle metodologie tecniche riguardanti il trasporto e deposito dei rifiuti di amianto nonché il trattamento, l'imballaggio e la ricopertura dei rifiuti contenenti amianto in discarica autorizzata di cui all'art. 6 della Legge 257, con il **D.M. 6 Settembre 1994** – vengono stabilite le normative e metodologie tecniche applicative circa la rimozione dei materiali contenenti amianto (allestimento del cantiere, decompressione, decontaminazione, smaltimento).

Sempre negli sviluppi attuativi della Legge 257, art.5 comma 1 lettera f), il **Decreto del Ministero della sanità 14 Maggio 1996** reca le normative e le metodologie tecniche per gli interventi di bonifica con particolare riguardo a quelli intesi a rendere innocuo l'amianto.

In materia di prevenzione e riduzione dell'inquinamento dell'ambiente causato dall'amianto, il **D.Lgs 17 Marzo 1995 n.114**, emanato in attuazione della direttiva 82/217/CEE, stabilisce i valori limite di concentrazione di amianto relativamente agli scarichi in atmosfera, agli effluenti liquidi ed alle attività di demolizione di manufatti e di rimozione di amianto o di materiali contenenti amianto.

La predisposizione dei Piani di bonifica e gestione dei rifiuti previsti dalle normative sopra citate, hanno messo in evidenza l'elevato rischio ambientale e sanitario correlato alla notevole presenza di amianto sul territorio nazionale.

La **Legge 9 Dicembre 1998, n.426**, il **Decreto 18 Settembre 2001, n.468** e la **Legge n. 179** del 2002, hanno consentito di individuare in tutta l'Italia i numerosi siti da bonificare di interesse nazionale in cui l'amianto è presente sia come fonte di contaminazione principale che secondaria.

In rispetto a tali normative, le aree contaminate da amianto sono state localizzate e perimetrare e per esse si è assicurata una prima copertura finanziaria per effettuare gli interventi di messa in sicurezza d'emergenza necessari per le situazioni di inquinamento più pericolose ed acute.

La **Legge del 23/3/2001 n.93** (art. 20) e il successivo **Decreto Ministeriale del 18/3/2003 n.101** hanno consentito la realizzazione di una mappatura completa della presenza di amianto sul territorio nazionale e degli interventi di bonifica più urgenti.

Per quanto riguarda lo smaltimento dei rifiuti, la materia è disciplinata dal Decreto Legislativo del 5 Febbraio 1997 n. 22, emanato in attuazione delle direttive 91/156/CEE sui rifiuti, 91/689/CEE sui rifiuti pericolosi e 94/62/CE sugli imballaggi e sui rifiuti pericolosi.

Tale decreto, tra l'altro, disciplina la gestione dei rifiuti, il recupero e lo smaltimento, opera una classificazione, interviene per la riorganizzazione del catasto dei rifiuti, regola il trasporto e stabilisce le competenze degli organi nazionale e regionali in materia di bonifica e ripristino ambientale dei siti inquinati. Demanda, tuttavia, a successive norme attuative le specifiche operative, i criteri e i limiti di ammissibilità che saranno, di volta in volta, stabiliti dagli organismi competenti nazionali e territoriali, ciascuno per la propria competenza.

Il **Decreto Legislativo del 13 gennaio 2003 n. 36**, in attuazione della direttiva 1999/31/CE, stabilisce i requisiti operativi e tecnici per i rifiuti e le discariche, le misure, le procedure e gli orientamenti tesi a prevenire o a ridurre le ripercussioni negative sull'ambiente, in particolare l'inquinamento delle acque superficiali, delle acque sotterranee, del suolo e dell'atmosfera, e sull'ambiente globale, nonché i rischi per la salute umana risultanti dalle discariche di rifiuti, durante l'intero ciclo di vita della discarica.

In sviluppo del decreto sopra citato, il Decreto Legislativo del 13 marzo 2003 stabilisce i criteri di ammissibilità dei rifiuti in discarica ivi compreso l'amianto e definisce anche i limiti di accettabilità e restrizioni per l'ammissione in discarica.

Con il successivo **Decreto Legge del 29 Luglio 2004 n. 248** sono disciplinate in maniera più completa il conferimento in discarica dei rifiuti contenenti amianto (RCA) ed il riuso, o meglio l'uso quale materia prima, di materiali derivanti dalla trasformazione dell'amianto.

Infine, sempre in materia di smaltimento dei rifiuti in discarica, il Decreto Ministeriale del 3 Agosto 2005, in attuazione dell'art. 7, comma 5 del Decreto legge 36/2003 sopra detto, stabilisce i criteri e le procedure di ammissibilità dei rifiuti, amianto incluso, nelle discariche definendo anche, per l'ammissibilità, i metodi di campionamento e le analisi.

In tale contesto normativo, che, pur nella sua complessità lascia tuttavia ancora aperti alcuni aspetti, si inquadra il Progetto LIFE-FALL che ha, tra i suoi obiettivi, anche la definizione di procedure analitiche per la determinazione quantitativa dell'amianto in percolati (attualmente non regolate da norme specifiche per le discariche), oltre all'accertamento del livello della loro pericolosità.

ITALIAN NATIONAL ASBESTOS COMMISSION AND ITS WORKGROUPS

M. Alessi

Department of Prevention and Communication, Ministry of Health.

In Italia il definitivo bando dell'amianto è stato sancito con l'introduzione della Legge 27 marzo 1992, n. 257 "Norme relative alla cessazione dell'impiego dell'amianto". Il provvedimento adottato vieta l'estrazione, l'importazione, l'esportazione, la produzione e la commercializzazione dell'amianto e dei prodotti contenenti amianto. A fondamento dell'azione normativa la legge ha previsto l'istituzione, presso il Ministero della sanità, di una Commissione "per la valutazione dei problemi ambientali e dei rischi sanitari connessi all'impiego dell'amianto". La costituzione della Commissione è stata quindi formalizzata con decreto del Ministero della sanità in data 1° luglio 1992 ed il suo insediamento effettivo è avvenuto il 26 novembre dello stesso anno. Nell'atto istitutivo il mandato è stato fissato per un arco temporale di tre anni. Successivamente, sperimentata la prima fase di attuazione della legge, constatata la vastità e la complessità delle tematiche affrontate, in continuo rinnovamento e divenire, sono stati affidati alla Commissione altri tre mandati, l'ultimo dei quali, considerate le latenze connesse all'effettivo insediamento operativo, è stato esteso a quattro anni (1996-1998; 1999-2001; 2002-2005). La composizione della Commissione, tenuto conto nel suo computo il Presidente, carica rivestita dal Ministro della sanità o da un suo Sottosegretario, è formata da 20 Membri rispettivamente designati, in numero congruo e predefinito di rappresentanza, tra gli esperti delle competenti amministrazioni dello Stato, degli Istituti/Enti scientifici nazionali; delle principali Organizzazioni Sindacali a livello nazionale; delle Organizzazioni delle Imprese industriali e artigianali del settore e delle Associazioni di protezione ambientale. Nell'arco della sua attività, la Commissione si è avvalsa, in tempi e modi diversi, della facoltà di ricorrere alla collaborazione di Istituti ed Enti di ricerca, portando a termine quei compiti che, tra quelli individuati tra le proprie competenze, richiedevano la predisposizione di vari disciplinari tecnici che sarebbero poi stati adottati, da parte dei Ministri competenti, con appositi decreti, in particolare, disciplinari, normative e metodologie tecniche sulle: a) modalità per il trasporto e il deposito di rifiuti di amianto nonché sul trattamento, l'imballaggio e la ricopertura dei rifiuti medesimi nelle discariche autorizzate; b) interventi di bonifica compresi quelli per rendere innocuo l'amianto. Tra queste azioni a varie riprese si è tentato di armonizzare e rendere operativamente realizzabile la standardizzazione delle metodologie di base per il monitoraggio e le analisi dell'amianto, compito risultato via via più complesso per la comparsa di nuove necessità conoscitive, una volta legate all'obiettivo di certificare materiali sostitutivi dell'amianto definiti "omologati", un'altra volta alla certificazione dell'avvenuta trasformazione dei rifiuti, al fine di ottenere una loro declassificazione di pericolosità e gestione in discarica,

o di garantire il loro recupero/riciclaggio, un'altra volta ancora dettati dall'esigenza di conoscere e valutare il rischio rappresentato dalla presenza di amianto nelle matrici di acque e suoli dei vari siti di interesse nazionale inseriti nei programmi di bonifica e recupero ambientale. A questo scopo, sono stati inizialmente definiti e pubblicati in decreto i parametri per la definizione dei "Requisiti minimi dei laboratori pubblici e privati che intendono effettuare attività analitiche sull'amianto" (D.M. 14 maggio 1996) e per la fase di realizzazione l'"Approvazione della scheda di partecipazione al programma di controllo di qualità per l'idoneità dei laboratori di analisi che operano nel settore amianto" (D.M. 7 luglio 1997). Per ogni metodologia analitica (MOCF, SEM, DRX e FTIR) sono stati definiti i programmi di qualità ed intercalibrazione, fino ad oggi mai avviati per oggettive difficoltà incontrate nel sostegno economico e gestionale, per la scarsità delle rispettive risorse necessarie. Ancora relativamente alle tematiche di monitoraggio ed analisi, durante l'ultimo arco temporale del mandato, la cui scadenza è fissata al 31 dicembre 2005, la Commissione, tra le altre attività, ha affidato l'incarico ad un Gruppo di lavoro specifico, costituito da membri interni ed esterni, di elaborare dei pareri tecnici sulle modalità di esecuzione di campionamenti ed analisi outdoor, per suoli e acque di siti inquinati con la potenziale presenza di amianto o fibre anfiboliche asbestiformi. Mancano infatti, in questo campo, specifici metodi di riferimento da impiegare nelle attività di monitoraggio. Il lavoro è ancora in corso di svolgimento e ad oggi risultano tracciati i criteri guida per l'impostazione delle indagini.

Session: Analysis in air

- | | |
|---------------|---|
| A. D. Jones | Current issues in asbestos fibre counting: changes in rules and national and international comparability |
| B. Tylee | The MDHS87 method and strategy for the discrimination of airborne fibres in the UK |
| G. Zanetti | Simplified analytical methods for a hard-mapping of asbestos in civil buildings |
| S. Massera | PCOM determination of airborne asbestos fibres: inter-laboratory comparison and validation proposal for an analytical method |
| M. Bruzzzone | Multi-year experience: a plan for the improvement of the analytical quality of 15 ligurian laboratories for the measurements of the concentration of the asbestos fibres in air (PCOM). |
| H. Kropiunik | Phase contrast microscopy versus scanning electron microscopy: critical discussion of asbestos monitoring methods based on empirical data from the Vienna international centre |
| A. Somigliana | Uncertainty assessment during PCOM filters observation |
| R. Stanescu | Physico-chemical methods to identify asbestos in occupational environment |
| E. Lauria | The necessity of SEM analysis in outdoor environment monitoring of airborne asbestos fibres |
| M. Bergamini | Monitoring of airborne fibres during remediation of the abandoned asbestos mines of Balangero and Corio |
| A. Cattaneo | Dimensional microscopic analysis of asbestos bundles released in atmosphere from an asbestos cement roof. |
| G. Cecchetti | Specific analytical techniques for asbestos analysis in air: comparison and evaluation |

CURRENT ISSUES IN ASBESTOS FIBRE COUNTING: CHANGES IN RULES AND NATIONAL AND INTERNATIONAL COMPARABILITY

AD Jones, MC Arroyo, P Brown, R Grosjean, BG Miller, B Tylee
Institute of Occupational Medicine – UK

INTERNATIONAL COMPARABILITY

Several European countries have proficiency testing schemes for laboratories that use phase contrast optical microscopy to evaluate concentrations of airborne asbestos fibres. However, there have been relatively few comparisons of counting levels in different countries. Such comparisons are needed as an essential part of harmonising performance across Europe.

A recent limited comparison through an interchange of slides (provided from national PT schemes) between six laboratories in three countries (Spain, Belgium and UK), suggested that there is good consistency in the counting levels between these three schemes. Consistency was also apparent from the counts of these laboratories in the long-running international comparison scheme, the *Asbestos Fibre Regular Informal Counting Arrangement*, (AFRICA). AFRICA includes 22 laboratories from 12 European countries and 11 laboratories from the other continents. We examine data from other laboratories in this scheme, to investigate international consistency between counting levels more widely, and report on the findings.

The recent incorporation of the unified WHO fibre counting rules for all fibre types into a European Directive has been an important step towards harmonisation. There is currently a period of transition to these new rules; some countries and laboratories have already switched to the new rules whereas others are about to do so. For some, the WHO rules should bring a small rise in fibre counts compared with their current counting rules. This transition may thus affect current international comparisons of fibre counts; we estimate the extent of the effect in the AFRICA data.

We make recommendations based on our shared experience of operating three national fibre counting PT schemes and two international PT schemes. The AFRICA scheme provides a sound basis for international comparisons of fibre counting, but there is a need for additional international exchanges of reference slides provided by the national PT schemes.

PREPARATIONS IN THE UK RICE SCHEME FOR THE CHANGE TO THE WHO ALL FIBRE COUNTING RULES

In the UK, preparations are being made for implementing the new World Health Organisation (WHO) all-fibre counting rules (for determining airborne asbestos concentrations from membrane filter samples) in April 2006. These preparations include a training exercise for laboratories in the UK national proficiency testing scheme, the *Regular Inter-laboratory Counting Exchanges* (RICE). They also involve recalibration of reference values for the samples used in RICE.

Both of these preparations involve determinations of the numbers of extra fibres that will be counted under the new rules. Under the present rules (the European Reference Method), some fibres touching particles are excluded; under the new rules fibres should be counted irrespective of contact with particles.

In the training exercise, about 160 RICE laboratories are applying both sets of rules to the same counting areas, and determining the number of extra fibres that become countable. Their results will be compared with those from "expert" laboratories in particular and with each other. These results will be part of the training recommended for UK analysts.

In the recalibration of reference values, all samples in the scheme are being evaluated by experienced laboratories to produce estimates of the percentage increase in count due to the extra countable fibres. This data will be used to define conversion factors for converting current reference values (which are based on medians of 15 or more counts by the current method) to values that are relevant to counts by the new rules.

Both exercises are due to be completed by the end of 2005. We will report on the analysis of data available by autumn 2005, to assess whether the conversion factors and training exercise are producing consistent information about the effect of the change of rule. Other issues involved in the transition will be discussed.

THE MDHS 87 METHOD AND STRATEGY FOR THE DISCRIMINATION OF AIRBORNE FIBRES IN THE UK

B. Tylee
Health and Safety Laboratory, Harpur Hill, Buxton, SK17 9JN, UK

The replacement of the European Reference Method (ERM) in Annex 1, of Council Directive 83/477/EEC by the World Health Organisation (WHO) method for the, "Determination of airborne fibre number concentrations", brings in a number

of changes in how fibre counting will be performed and interpreted. The initial effect of the changes is to increase the number of "regulatory" fibres counted but the WHO method also allows for fibre discrimination to take place when comparing exposures to the control limit. Fibre discrimination will therefore tend to reduce the fibre count by allowing non-asbestos fibres to be excluded from the count. This change in evaluating the fibre number concentration is consistent with the prohibition of the supply and use of asbestos in the EU and the cessation of the manufacturing of asbestos containing materials (ACMs). The amending directive 2003/18/EC now focuses on management and removal of 'in place ACMs', where it can no longer be assumed that the fibres visible by phase contrast microscopy are necessarily asbestos fibres

The Health and Safety Executive through its Committee on Fibre Measurement (CFM) develops and publishes methods for the determination of hazardous substances. MDHS 87 was developed in response to the need to discriminate between fibre types and outlines the recommended strategies and method used in the UK. An outline of the MDHS 87 method is given along with examples of successful strategies that have been used, to overcome the presence of non-asbestos fibres.

Examples of where this discrimination may be applied include exposure assessments of work done on chrysotile-containing decorative coatings where both chrysotile and calcium sulphate 'fibres' can be encountered, asbestos removal in the presence of glass or ceramic fibres, and clearance testing in areas which have previously stored paper and textile fibres.

The UK RICE (asbestos-counting fibre proficiency) programme plans to introduce as an optional feature sets of samples for the assessment of laboratories when undertaking fibre discrimination.

The presentation will aim to demonstrate and discuss what level of discrimination can be achieved by light microscopy, before having to resort to off-site laboratory based analysis methods, such as electron microscopy and energy dispersive X-ray analysis, and how performance assessments can be made.

SIMPLIFIED ANALYTICAL METHOD FOR A HARD-MAPPING OF ASBESTOS IN CIVIL BUILDINGS

C. Cazzola¹, C. Clerici¹, G. Zanetti¹, E. Basti², E. Braghini²

¹ Politecnico di Torino- Dipartimento di Ingegneria del Territorio, dell'Ambiente e delle Geotecnologie

² Agenzia Territoriale per la Casa della Provincia di Torino

The ATC (Agenzia Territoriale per la casa della Provincia di Torino) is a public institution who has the task of supplying cheap apartments to poor people. It, also, has to manage its properties and those that other public institutions have entrusted to it.

Therefore ATC is owner of a large building patrimony, that is summarized in the following table.

Table 1 Analysed ATC patrimony

ATC patrimony	Quantity	Analysed samples	Asbestos containing samples
Buildings	1285	7151	1904
Thermal station	458	3333	345
Empty flats	638	920	397

A big part of this patrimony has been build in the years '50-80, when asbestos materials were largely employed both for industrial building and for house building.

The law 257/92: "Cessazione dell'uso dell'amianto" obliges the location of friable asbestos containing materials in the buildings, because it is one of the most hazardous situations of exposure, but it doesn't clearly take care of asbestos in hard products.

The following D.M. 06/09/94 makes the location of asbestos obligatory for every kind of asbestos materials in civil buildings; as a matter of fact the mapping is the first step in order to respect the two obligations of thus D.M.:

- the evaluation of the risk
- the programme of management and custodial control

Following the legislative orders the ATC has started a mapping of asbestos materials in its building patrimony. This activity has been carried out with the help of Dipartimento di Georisorse e Territorio di Torino, who has coordinated the scientific research and the laboratory' s analysis.

Asbestos has had a large employment in the building field, so you can found asbestos material both in manufactured articles used in building and in manufactured articles used for plant engineering.

Some examples could be:

- for the first type: cement roofing (tiles), asbestos floor tiles, asbestos insulation board, thermal insulation and acoustical control (sprayed asbestos)
- for the second type: asbestos pipes, asbestos tape, asbestos impregnated paper product used for pipe and boiler insulation, fire proofing..
- above all asbestos materials used for strange products (flowerpots) and abandoned asbestos materials.

The building patrimony of ATC is very large, so it has been necessary to plan some quick and cheap analysis.

It must be taken into account the fact that for the mapping of asbestos materials we don't need a quantitative analysis but only a qualitative analysis. It is also important to know if a material contains an amphibole asbestos or chrysotile, because the first one spread in the air easier than the second one.

PLOM (polarised light optical microscopy) associated with PCOM (phase contrast microscopy with chromatic dispersion) is a good method for a qualitative analysis of asbestos materials, in fact it has the following characteristics:

- low instrumental cost (less expensive of other methods)
- short time of analysis
- it's not important the bigger defect of the microscopic analysis, that is the transformation of the results from qualitative analysis to quantitative analysis, because in this case a qualitative response is sufficient
- the problem of the small quantity of analysed sample can be solved taking a large number of samples, so to obtain a representative result
- in order to see the fibres with optical microscope, it is necessary to liberate the fibres from the matrix with some simple chemical treatments

The used chemical treatments are different according to the material, we wish to analyse.

- for cement materials (asbestos cement): grinding with an hard-duty mortar \Rightarrow bite with hydrochloric acid \Rightarrow filtration \Rightarrow oven drying
- for friable materials: manual research of the fibres with a stereomicroscope \Rightarrow sometimes washing with water on a sieve or cleaning of fibres directly on the slide, after immersion in oil using the glass rod.
- for materials with non cementitious solid matrix: grinding with a mortar \Rightarrow search of the fibrous aggregate with the stereomicroscope \Rightarrow cleaning of fibres directly on the slide, after immersion in oil using the glass rod.
- for vinyl floors: combustion at around 300°C \Rightarrow grinding with a mortar \Rightarrow bite with hydrochloric acid \Rightarrow filtration \Rightarrow oven drying
- for powdery materials: sizing with an automatic sieving machine (the rotating motion of the sieves make the fibres aggregate among them, so that they can be easily separated), the size classes are studied one by one.

The samples for the microscopic observation are prepared dispersing small quantities of material (obtained from the previous treatments), deposited on a slide, in a dipping oil with a known refractive index. In addition to the eugenol (liquid with a refractive index of 1.54, used for a general evaluation of the sample), the liquid (Cargille Laboratories) with refractive index 1.550, has been usually employed in order to recognise the chrysotile asbestos. PLOM has been used for the search of amphibole asbestos; when there is a doubt, it has been used PCOM with a Cargille liquid apt to recognise this kind of amphibole (for example to recognise amosite by means of chromatic dispersion the Cargille liquid with refractive index: 1,670 has been used).

The following figures show the efficiency of the acid treatments in the case of asbestos cement (fig.1-2) and of vinyl floor fig.(3-4).



Fig. 1 Not-treated asbestos cement containing chrysotile and crocidolite. PLOM. Short side of the photo 0.94mm.



Fig. 2 HCl-treated asbestos cement containing chrysotile and crocidolite. PLOM. Short side of the photo 0.94mm.

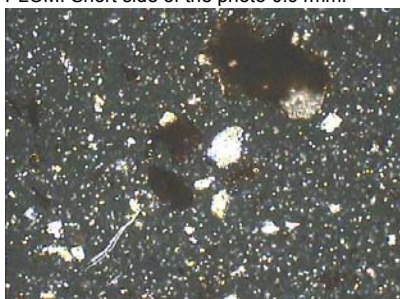


Fig. 3 Not-treated vinyl floor containing chrysotile. PLOM. Short side of the photo 0.94mm.

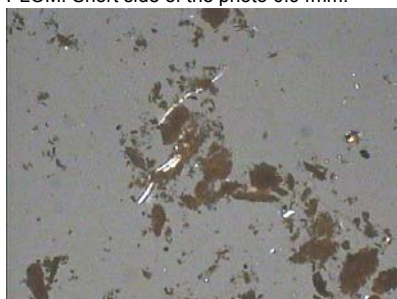


Fig. 4 Treated vinyl floor containing chrysotile. PLOM. Short side of the photo 0.94mm.

The results of the mapping are reported in the following tables.

Table 2 Number of buildings with or without asbestos

Total inspected buildings	1285	100.0%
Buildings with asbestos	407	31.7%
Buildings without asbestos	878	68.3%

Table 3 Localisation of in use or abandoned asbestos materials

Total buildings with asbestos materials	878	100.0%
Buildings with in use asbestos materials (cement roofing tiles, pipes...)	607	68.4%
Buildings with both in use and abandoned asbestos materials (pipes and piece of pipes and tiles)	250	29.3%
Buildings with only abandoned asbestos material	21	2,3%

PCOM DETERMINATION OF AIRBORNE ASBESTOS FIBRES: INTER-LABORATORY COMPARISON AND VALIDATION PROPOSAL FOR AN ANALYTICAL METHOD

E. Incocciati, S. Massera

INAIL CONTARP: Italian Workers' Compensation Authority, Risk Assessment and Prevention Central Technical Advisory Department – Rome, Italy

The Membrane Filter Method (MFM) applied to Phase Contrast Optical Microscopy (PCOM) is one of the analytical methods provided by the Italian laws concerning sample surveys and assessments of professional exposure to the asbestos [1,2].

Despite the low costs and the promptness of analysis, PCOM is affected by a large variability in fibre counting. Italian laws don't provide validation parameter values about this kind of analysis neither national fibre proficiency testing (PT) schemes have been started yet.

A decree had foreseen the activation of national ring tests [3] but the only initiatives taken up to date have been carried out by little groups of laboratories or local institution without any national control [4, 5]. This kind of studies are aimed to evaluate laboratory performances as done by national and international PT schemes for asbestos fibre counting operating in the world [6].

Variability in counting can be controlled by adopting uniform analytical procedures; moreover a common formation program can assure homogeneous rules for fibre counting on filter.

Starting from law in force and international standards [7, 8, 9] INAIL (Italian Workers' Compensation Authority) has carried out a project aimed both to evaluate the performance of its laboratories and to begin to validate its analytical method for asbestos fibre counting by PCOM. This paper describes steps, criteria and results of the first two years of this still in progress study.

Thirteen INAIL laboratories, operating all over the national territory, have taken part to a PT scheme. The study has been planned as a collaborative trial: each participating laboratory adopts the same method to analyse the test samples and produces its counts according to a well defined protocol.

The project has begun with a formation meeting within analysts involved in order to harmonise the operating procedure and fix a common method in applying the counting rules. The scheme has foreseen sample exchange and evaluation of analytical performance of each laboratory taking part in the project.

Samples have been delivered according to two rounds composed by six slides. Slides have been chosen among filters coming from surveys in workplaces in order to include a wide range of fibrous materials (chrysotile, amosite and vitreous fibre) with different deposition density on membrane. High and low fibre density have been distinguished on the base of a target value of 100 ff/mm². On the whole 12 samples have been provided and 156 PCOM analysis have been collected.

According to Italian laws, all the objects having the same dimensional characteristic (Length > 5µm, Width < 3µm, Length/Width ratio > 3) are countable as "asbestos fibre". For this reason and because of the lack of certified reference materials, results and laboratory performances have been classified with reference to the total number of countable fibres on filter without distinguishing between the different kinds. Counting rules of DM 6/9/94 have been adopted. Analysts have been asked to count the samples according to this rules and to express their results in terms of ff/mm².

The RICE (Regular Inter-laboratory Counting Exchange) scheme [10], operating in the UK for almost 20 years, have been used to evaluate the analyst performances. The reference value for each slide has been assumed equal to the arithmetic mean value of the counts of the results given by the 13 laboratories.

According to DM 14/5/96 laboratory performances have been distinguished between *satisfactory* and *unsatisfactory*. Each laboratory has been classified as *satisfactory* if the set time limits (4 working days) have been observed and if, including counts of the two program rounds, results of each analysis have been evaluated as *good* or *sufficient* (Table 1).

Table 1 - RICE criteria for classifying results in fibre counting PT schemes.

$V < (\sqrt{R-2.34})^2$ or $V > (\sqrt{R+3.30})^2$	Insufficient
$(\sqrt{R-2.34})^2 < V < (\sqrt{R-1.57})^2$ or $(\sqrt{R+1.96})^2 < V < (\sqrt{R+3.30})^2$	Sufficient
$(\sqrt{R-1.57})^2 < V < (\sqrt{R+1.96})^2$	Good

(R = reference value for analysed sample; V = result of the single count to be evaluated).

At the end of each round, all results have been critically reviewed in order to mark out the difficulties found during the analysis (counting rules applied, setting and correct adjustment of the microscope, ecc.) and to assess the laboratory performances according to RICE criteria.

Moreover the scheme has been aimed to study the analysis protocol performance in terms of accuracy and expanded uncertainty, even if referring only to the counting phase (not to the sampling).

The uncertainty has been calculated following a top-down approach based on the reproducibility data employment. Results have been statistically processed according to a method already adopted on drinkable water analysis [11].

Through 3 different statistical methods (Z-score, Huber, Cochran) presence of outliers has been verified and acceptable results have been selected. The accuracy of the interlaboratory test has been verified through a t-test and reproducibility standard deviation (combined standard uncertainty) has been obtained. This last parameter, multiplied by a coverage factor, based on the level of confidence desired, has given the value of expanded uncertainty to be associated to analysis result.

Counts collected on a test sample of amosite at low density (mean value: 40 ff/mm²) have been statistically processed in order to evaluate the expanded uncertainty.

Table 2 shows results of the two rounds in terms of standard deviation (SD) and variation coefficient (CV) of data. Results of data classified according to RICE criteria are illustrated too.

Table 2 - results of the counts of the rounds.

Slide n°	1	2	3	4	5	6	7	8	9	10	11	12
Mean value (ff/mm ²)	85	36	86	47	86	48	105	25	19	32	216	41
SD	22,0	22,2	23,3	11,3	22,1	24,8	41,4	11,0	6,5	4,9	41,5	13,3
CV	0,26	0,62	0,27	0,24	0,26	0,51	0,39	0,44	0,35	0,15	0,19	0,32
No of measures <i>good</i>	12	9	11	12	11	10	9	12	13	13	11	12
No of measures <i>sufficient</i>	1	2	2	1	1	2	3	1	-	-	2	1
No of measures <i>insufficient</i>	-	2	-	-	1	1	1	-	-	-	-	-

At the end of the first round performances of 7 laboratories have been classified as *satisfactory* while in the second round this number has increased to 11.

The expanded uncertainty has been calculated on the test slide containing amosite (3 data have been classified as outliers according to the statistical test results): the final result for fibre density was 40±21 ff/mm².

Table 2 shows that the standard deviation observed are similar (the same order of magnitude) to the ones reported on international standardised methods [7].

Moreover participating laboratories have improved their performances from the first to the second round. This improvement is probably due to the effectiveness of sharing formation among analysts operating in different laboratories.

The uncertainty obtained in the examined sample confirm that MFM PCOM is affected by a large variability of results due to several sources of random and systematic errors. It's now appropriate to extend this determination to other kinds of material and to slides having different fibre density.

References

- [1] Decreto Legislativo 15 agosto 1991 n° 27. *G.U. Supp. Ord.* 200 (1991).
- [2] Decreto del Ministero della Sanità 6 settembre 1994. *G.U. Supp. Ord.* 288 (1994).
- [3] Decreto del Ministero della Sanità 14 maggio 1996. *G.U. Supp. Ord.* 251 (1996).
- [4] Camilucci L., Campopiano A., Casciardi S., Fioravanti F., Ramirez D. *Fogli d'Informazione ISPESL*, 2 (2000).
- [5] A.Somigliana, C. Dozio, M. Nardini, A. Qualini, CV. Gianelle, G. Colombo, G. Cattaneo. *Giornale degli Igienisti Industriali* 29, 4 (2004).
- [6] A. D. Jones, M.C. Arroyo, R. Grosjean, B. Tylee, B.G. Miller, P. Brown. *Ann. Occup. Hyg.* 49, 4 309-324 (2005)
- [7] NIOSH - National Institute for Occupational Safety and Health. Method 7400, issue 2. *NIOSH Manual of Analytical Methods 3rd Edn* 84-100 (1994).
- [8] WHO. Methods of monitoring and evaluating man-made mineral fibres, World Health Organization, Regional Office for Europe, Copenhagen (Euro Report and Studies n. 48).
- [9] UNI EN 482. (1998).
- [10] Brown P.W., Crawford N.P., Jones A.D., Miller B.G., MacLaren W.M. *Ann. Occup. Hyg.*, 38: 387 (1994).
- [11] ARPA Emilia Romagna. Linee guida per la validazione dei metodi analitici e per il calcolo dell'incertezza di misura. Accreditamento e certificazione. Bologna, Labanti & Nanni, (2003).

MULTI-YEAR EXPERIENCE: A PLAN FOR THE IMPROVEMENT OF THE ANALYTICAL QUALITY OF 15 LIGURIAN LABORATORIES FOR THE MEASUREMENTS OF THE CONCENTRATION OF ASBESTOS FIBRES IN AIR (PCOM)

M. Bruzzone¹, G. Capannelli², L. Cortesogno³, L. Gaggero³, T. Valente⁴

¹ASL 3 Genovese – U.O. PSAL

²Università Genova, DCCI

³Università Genova, Dip. TERIS

⁴Università Genova, DIMEL – Sez. Medicina del Lavoro

The project, which spread over several years, begun in 2000 and was re-financed after the first positive issue by the Administration of the Liguria Region, and was based on the voluntary participation of practically the totality of Ligurian Laboratories active on the subject.

This plan has been developed in strong interaction with three Genoa University structures: Department of Chemistry and Industrial Chemistry (DCCI), Department of the Earth and its Resources (DIPTERIS) and Legal Medicine Department – Occupational Medicine (DIMEL - Section Occupational Medicine).

The project was realized in two series, in 2000-2001 and 2002-2003, with ten seminar discussions for the comparison of sampling techniques for the monitoring of asbestos fibres in air, the preparation of membrane filters and laboratory counting. Concurrently Inter-Laboratories circuits of specimens' analysis (microscope counting) had been organized, carried out following a criterion that guaranteed the anonymity of the participants.

The participants Laboratories were: the above-mentioned University Departments, some public structures (or control structures or public companies) and other private laboratories (some associated to asbestos removal company, other "pure" analytical laboratories).

The interaction between different origins and tasks, and the use of a uncommon location, compared with usual ones where "control structure and controlled companies" usually face each other, that is to say the University classrooms - had a positive effect on the contents and freedom of argument.

Discussions on sampling techniques, specimen preparation and mounting was animated between all participants, always twenty persons or more, and led to the preparation of a form to collect basic information on sampling, and a photo-diagram on membrane mounting and counting analysis lay-out (figure).

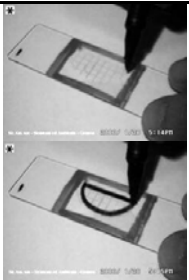
Phase	Instructions	Notes	Image
Contour effective membrane filtration area	With a permanent marker outline approximately the effective filtration area of the membrane (better inner then outer). In this way it will be easier to remain on the deposit surface.	This operation is always useful, but fundamental when: <ul style="list-style-type: none"> • The membrane filter had a short sampling time • The membrane is from a clean ambient, the deposit "shadow" is invisible <p>In these situations it's easy to go of useful area without realizing.</p>	

Figure 1 – example of photo-diagram on sampling preparation

At the same time three session of inter-laboratory counting of specimens were organized. Four Laboratories (the Universities and our PSAL laboratory) selected some of their specimens, collecting a set of 4 each session; each participant laboratory analysed the four samples and submitted the results at the Legal Medicine Department – Occupational Medicine that collected and rendered anonymous all the results in order to make the statistical analysis. All specimens had a load of fibres ranging between 5 and 45 fibres/mm².

Table 1 – concise statistic of total inter-Laboratories counting

	2000	2001	2002
Rating	I° Series	II° Series	III° Series
	%	%	%
Insufficient	15%	19%	12%
Sufficient	11%	17%	15%
Good	53%	52%	74%
Rejected	21%	12%	0%

Insufficient = outer of 0,5 and 2,0 times of median value

Sufficient = inner of 0,5 and 2,0 of median value

Good = inner of 0,65 and 1,65 of median value

Rejected = very far from range limit values (outliers?)

The number of specimens in this project is small, insufficient to obtain an acceptable and reliable level of statistical analysis, but this may be the beginning of a new and more accurate project. Nevertheless it is possible to list some positive effects on the Laboratories:

- a. mutual knowledge between laboratories and, mostly, between operators;
- b. the creation of an opportunity of confrontation between public and private laboratories, exclusively on a scientific basis;
- c. the creation of a report, on these topics, that may represent a reference manual for all Laboratories, whether participants or not in project;
- d. the collection and sharing of major recoverable methods;
- e. Form draw up for different stages and analysis: sampling form, MOCF counting form, SEM counting form
- f. The Inter-Laboratory analysis demonstrated that, without any changes on laboratory equipment, it is possible to improve the quality and reliability of analysis.

Reports have been published on a monographic supplement of the Liguria Region Bulletin and on the DIPTERIS web site (<http://www.dister.unige.it/attiv/amianto/>).

- [1] Metodo AIA N° 1 (RTM1) – “Metodo di riferimento per la determinazione delle concentrazioni di fibre d'amianto sospese nell'aria sui luoghi di lavoro mediante microscopia ottica (metodo del filtro a membrana)” – *AIA, Asbestos International Association* – 68 Gloucester Place, London W1H 3HL, England
- [2] Metodo “D.M. 16.10.86” - (*G.U. 29 novembre 1986, n. 278*)
- [3] Metodo “D.Lvo 277 – Allegato V” - (*G.U. 27 agosto 1991, n. 200, suppl. ord.*)
- [4] Metodo “D.M. 6.9.94 – Allegato 2” - (*G.U. 10 dicembre 1994, n. 288, suppl. ord.*)
- [5] NIOSH - “Asbestos and other fibers by PCM – Method 7400” – *NIOSH Manual of Analytical Methods (NMAM)*, fourth Edition 15.8.1994
- [6] WHO - Determination of airborne fibre number concentrations - 1997
- [7] Ogden T.L. - “The reproducibility of fiber counts” - Health and Safety Executive Research Paper 18 (1982)
- [8] Abell, M., Shulman and P. Baron “The Quality of Fiber Count Data” - *Appl. Ind. Hyg.*, 4, 273-285 (1989)
- [9] Johnston A.M., Jones A.D., Vincent J.H. - “The influence of external aerodynamic factors on the measurement of the airborne concentration of asbestos fibres by the membrane filter method” – *Ann. Occup. Hyg.*, Vol. 25 n° 3, pp. 309-316 (1982)
- [10] Arroyo M.C., Rojo J.M. - “National versus international asbestos fibre counting schemes: comparison between the Spanish interlaboratory quality control program (PICC-FA) and the Asbestos Fibre Regular Informal Counting Arrangement (AFRICA).” *Ann. Occup. Hyg.*, 42, 97-104 (1998)
- [11] Marconi A., Falleni F., Campanella E. - “Confronto tra microscopia ottica in contrasto di fase e microscopia elettronica a scansione per l'analisi delle fibre di amianto aerodisperse in ambiente di ufficio” – *Med. Lav.* 1993, V. 84(3) 211-216
- [12] Marconi A., Campanella E., Ciccarelli C., Ripanucci G., Caretta D., Patroni M. - “Studio pilota per un confronto interlaboratorio dei risultati ottenuti con il metodo del filtro a membrana applicato a campioni con densità di fibre di amianto” – *Giornale degli Igienisti Industriali* 1991, Vol. 16 n. 2
- [13] Mineralogical Association of Canada. Short course in mineralogical techniques of asbestos determination, Quebec, May 1979, Ed.: RL Ledoux
- [14] Brown P.W., Jones A.D., Miller B.G. - Developments in the RICE Asbestos Fibre Counting Scheme, 1992 - 2000 - *Ann. occup. Hyg.*, Vol. 46, No. 3, pp. 329-339, 2002

PHASE CONTRAST MICROSCOPY VERSUS SCANNING ELECTRON MICROSCOPY: CRITICAL DISCUSSION OF ASBESTOS MONITORING METHODS BASED ON EMPIRICAL DATA FROM THE VIENNA INTERNATIONAL CENTRE

Heinz Kropiunik

Aetas Ziviltechniker GmbH, Kardinal Rauscher-Platz 4, 1150 Wien

The asbestos removal at the Vienna International Centre (VIC), one of 4 headquarters of the UN, might be the biggest asbestos removal exercise worldwide. It started 1999 with a pilot project in one regular floor and should be finished in the year 2010.

Due to the international character of the VIC, there had to be considered different asbestos removal standards during the planning procedure in order to provide a common approach between all parties as well as between the technical experts coming from different countries.

One issue of discussions was the method of asbestos monitoring to be conducted during the asbestos removal project. On the one hand, monitoring methods based on scanning electron microscopy (SEM) had to be considered in any way according to Austrian laws and standards. On the other hand, in most of all countries where asbestos removal is part of everyday occurrence, monitoring standard is based on phase contrast microscopy (PCOM). While executing the pilot project in one of 100 regular floors in 1999 in order to gather experience for the planning and tendering procedure for the overall project it was decided also to monitor by SEM and by PCOM in parallel in order to get a clear view on what is necessary and what is significant. During 3 months of time of this pilot project there were executed appr. 100 air measurements based on the Austrian SEM-Method (ÖNORM M 9405) and appr. 650 air measurements based on a PCOM-Method (NIOSH 7400). The results were really astonishing and were responsible for the decision to release air

monitoring according to PCOM-Methods totally. While SEM-monitoring is able to detect pure asbestos fibres at a detection limit of approximately 290 fibres / m³, PCOM-monitoring cannot distinguish between asbestos fibres, MMMF or organic fibres and the detection limit is not lower than approximately 10.000 fibres / m³. According to the results of PCOM-monitoring in comparison with those of SEM monitoring it was found that PCOM-monitoring did not allow a statement of any asbestos contamination in air, but only of a general fibre load. The main influence on the monitoring results of PCOM-measurements was the activity on site of sampling. On the other hand, PCOM-monitoring did not show significant higher results while SEM-monitoring signalized increased results above of the clearance limits. All results of measurements that have been executed by PCOM- and SEM-monitoring at the same time and on the same site, have been put in comparison to each other. The outcome of this comparison is shown below:

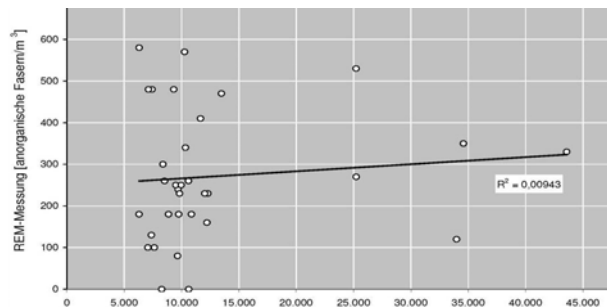


Figure 1: Comparison of results of PCOM- and SEM-monitoring

Due to the very low correlation between the results of these two monitoring methods it was found, that PCOM-monitoring can not be a useful method for detecting asbestos fibre concentrations as clearance measurements after an asbestos removal exercise. The detection limits and the philosophy of PCOM-monitoring might be an appropriate method for undertaking occupational measurements at work places where people are working with asbestos and everyone can await that detected fibres should be asbestos fibres only. For monitoring in our environment and for indoor monitoring, e.g. after finishing an asbestos removal exercise and before removing enclosures and NPU's, SEM monitoring should be the only acceptable method.

UNCERTAINTY ASSESSMENT DURING PCOM FILTER OBSERVATION

A. Somigliana, S. Albiero, M. Orsi, A. Quaglini

Electron Microscopy Division - Air Unit, Department of Milan – ARPA Lombardia

The evaluation of measurement uncertainty is one of the major issues that a test laboratory must face during the accreditation phase, according to ISO 17025 standard. This work has the goal to theoretically evaluate the uncertainty related to the analytical section of the PCOM analysis of airborne fiber concentration estimate as indicated by the DM 6/9/94 (Italian Law), without taking into account the air sampling. A theoretical evaluation is necessary because, nowadays, for this kind of analysis, there is not on the market any certified sample with a known concentration of fibers for mm². The reference standards for this work are the ISO GUM and the QUAM 2000 standard.

Measurand description

To estimate the fiber concentration for analyzed filter fraction, one has to count the visible fibers (N_f) in a number N_C of fields of view, of area a (inside at the Walton-Beckett graticule), randomly chosen over a filter of effective area A .

The number of fibers for the analyzed filter fraction (C) is given by the formula:

$$C = N_f \times A \times \frac{1}{a} \times \frac{1}{N_C}$$

Uncertainty components evaluation: $u(x)$

The quantities that describe the measurand are independent of each other. Given that in the concentration evaluation formula there are multiplication and division operations only, for the simplicity of the combined uncertainty estimate through the uncertainty propagation law, the single uncertainty components will be expressed as relative standard uncertainties ($u(x)/x$).

Relative standard uncertainty of A (filter effective area): $u(A)/A$

The filter effective area was estimated using a Vernier caliper to measure the diameter (d) of the deposition spot of the dust on the filter. The length measurement uncertainty components of a Vernier caliper are: the Vernier caliper accuracy as given by the supplier (0.1 mm), the reproducibility (0.1 mm) and the reading uncertainty (0.5 mm).

The relative standard uncertainty of A , in our laboratory, is overall estimated as $u(A)/A = 0.05$.

Relative standard uncertainty of a (field of view area - Walton-Beckett graticule): $u(a)/a$

The Walton-Beckett graticule casts a circular image over the field. The area a of this image defines the field of view over the filter. The graticule diameter was estimated by means of a calibrated stage micrometer. The overall relative standard uncertainty of the diameter measurement was equal to 0.017, from which the relative standard uncertainty $u(a)/a$ is derived as equal to 0.035

Relative standard uncertainty of N_C (net field of view number): $u(N_C)/N_C$

The uncertainty in N_C represents the observed field number counting error that may be made by the operator during the analysis. It can be linked to distraction, to interruption and subsequent restart of the analysis, to field signing error. In our laboratory, we read a total of 400 fields for the whole analysis. Considering an uncertainty $u(N_C)$ of about 8 fields over 400, the relative standard uncertainty of N_C becomes $u(N_C)/N_C = 0.02$.

Relative standard uncertainty of N_f (counted fibers' number): $u(N_f)/N_f$

Theoretically the Poisson distribution defines the fiber counting fluctuation that results from a random choice of the observed fields over the filter. This is the minimum uncertainty intrinsic to the *membrane filter* method (N_{fp}). To this component one can add the variability among laboratory operators both in regards to the ability to identify and recognize fibers in samples differently loaded with dust or interfering particles (*visual acuity*), and in regards to the counting rules developed by the single operator (agglomerate interpretation, fibers in contact with larger or smaller particles, fibers partially contained in the field of view, etc.). This second component, from now on called inter-operator or intra-laboratory uncertainty (N_{fa}), was experimentally estimated in our laboratory.

Relative standard uncertainty inter-operator: $u(N_{fa})/N_f$

After a period of *internal re-alignment* regarding individual counting rules, a complex sample was analyzed by all the operators over the same reading fields. The inter-operator uncertainty was estimated as the standard deviation of the total fibers counted by the various operators with the following result: $u(N_{fa}) = 5.4$, given $N_{fa} = 38$. Thus the relative standard uncertainty of N_{fa} results 0.14.

Relative standard uncertainty intrinsic to the counting method: $u(N_{fp\pm})/N_f$

Given that the Poisson distribution is asymmetric, we separately evaluated the upper and lower uncertainties. For each N_f value, they were estimated as the half difference in absolute value between the upper and lower 95% Poisson confidence limits and N_f ¹.

Relative standard combined uncertainty evaluation: $u_C\pm(C)/C$

Using the uncertainty propagation law, the relative standard combined uncertainty was evaluated as a function of N_f .

$$\frac{u_{C\pm}(C)}{C} = \sqrt{\left(\frac{u(A)}{A}\right)^2 + \left(\frac{u(a)}{a}\right)^2 + \left(\frac{u(N_C)}{N_C}\right)^2 + \left(\frac{u(N_{fa})}{N_f}\right)^2 + \left(\frac{u(N_{fp\pm})}{N_f}\right)^2}$$

Relative expanded uncertainty evaluation: $U(C)/C$

The expanded uncertainty is required to provide an interval which may be expected to encompass a large fraction of the distribution of values which could reasonably be attributed to the measurand.

The 95% confidence limit is normally estimated and it is obtained multiplying the combined uncertainty by a coverage factor k ; that is $U(C)/C = k \times u_C(C)/C$

In our case the distribution is not normal and the combined uncertainty was estimated mainly by statistical considerations. In such case the ISO GUM suggests to estimate k on the basis of the measurement degrees of freedom effective number ν_{eff} .

After applying the suggestions reported in the ISO GUM standard [Appendix G, prospect E.1 and prospect G.2], an adequate coverage factor, valid for every N_f values, is derived as equal to 2.1.

Relative expanded uncertainty: $U(C\pm)/C$

In table 1 we report the relative expanded uncertainties of C , upper and lower, evaluated for a few N_f values.

Table 1: relative expanded uncertainties for some N_f values

N_f	$U(C-)/C$	$U(C+)/C$
1	1.07	4.81
2	0.98	2.76
5	0.78	1.44
10	0.64	0.94
20	0.52	0.66
50	0.42	0.47
100	0.38	0.39

Table 2: CV (%) comparisons

N_f	CV (%) WHO 97	CV % Mean \pm
5	49	53
7	43	44
10	37	38
20	30	28
50	25	21
100	22	19

¹ If the known uncertainty is associated to a 95% confidence limit, to make it compatible with the other uncertainty components (standard uncertainties), it is possible to use its half value in the total uncertainty evaluation. [QUAM 2000].

95% confidence limits

They are estimated by the formula:

$$L_{\sup/\inf} = C \times \left(1 \pm \frac{U(C \pm)}{C}\right)$$

Comparison with other studies

As a comparison with other methods found in literature, in table 2 we report, for different N_f values, the average coefficients of variation evaluated here together with those reported on the WHO-1 method, that takes into account only the intra-laboratory fluctuations, or the inter-operator ones in the laboratories where adequate quality control schemes are carried out. The values presented are consistent with those reported on the WHO-1 methodology. To compare our data with the intra-laboratory reproducibility estimated in semi-empirical way by Ogden (1982) and in the NIOSH 7400 method, we also evaluated the 90% confidence limits as a function of N_f . These are reported in figure 1. The differences between the limits estimated with the two methods are about 5% for the lower limit and about 10% for the upper one (N_f between 5 and 100).

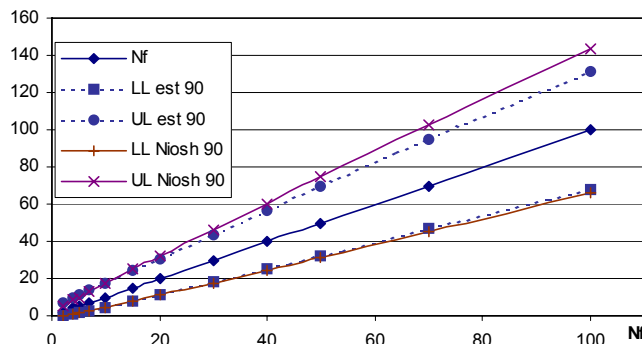


Figure 1 - 90% confidence limits' comparison

References

- ISO GUM: The ISO Guide to the expression of uncertainty in measurement (1995)
 QUAM 2000: Eurachem/CITAC Guide CG4 "Quantifying Uncertainty in Analytical Measurement" (2000)
 WHO-1: "Determination of airborne fiber number concentrations" WHO (1997)
 Ogden (1982): "The reproducibility of asbestos counts" Research Paper 18 HSE (1982)
 NIOSH 7400: "Asbestos and other fibers by PCM" Niosh Manual of Analytical Method (1994)

PHYSICO-CHEMICAL METHODS TO IDENTIFY ASBESTOS IN OCCUPATIONAL ENVIRONMENT

R. Stanescu Dumitru¹, E. Ruse²

¹ Institute of Public Health, Bucharest, Romania

² Polytechnic University, Faculty of Applied Chemistry and Materials Science, Bucharest, Romania

This paper reports a comparison between two physico-chemical methods used to identify asbestos presence in the airborne areas, namely Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM).

Materials and methods

Air asbestos samples were collected from working environment on cellulose membrane filters of 0.8 μm pore size using personal samplers. The samplers were collected from two technological processes: manufacturing of the insulation elements (10 samples) and manufacturing of asbestos fabrics (10 samples).

In order to identify asbestos presence in samples by FT-IR spectroscopy, the standard KBr disc technique was used. The sample filters loaded with dust were placed in porcelain crucibles, loosely covered and ashed in muffle furnace for 2 h at 600°C. 300 mg KBr was added to 0.1 mg sample ash. The mixture was transferred to a 13-mm pellet die, which was pressed using standard technique.

The spectra for both airborne collected samples and UICC standards of chrysotile, crocidolite and amosite were recorded in the range 4000-400 cm^{-1} . The UICC asbestos standard samples were furnished by International Agency for Research on Cancer, Lyon, France. A Jasco 460 Plus FT-IR spectrometer was used. The sample and standard spectra were then compared [1,2]. A resolution of 4 cm^{-1} was used.

In the case of SEM technique, we used a Philips 515 scanning electron microscope connected to an energy dispersive X-ray microanalysis system (EDXS). In order to analyze asbestos by SEM, we used the technical method no. 2 (RTM2) recommended by Asbestos International Association [3]. Sample preparation consisted of carefully cutting 1 cm^2 sample of each filter. The sample stuck to stubs and then covered by carbon and copper to improve conductivity. Samples were observed at a magnification between 2,000-10,000 X. Chemical analysis of asbestos fiber was performed by means of

microanalysis system EDXS. X-ray spectrum from 0-20 KeV was obtained for each fiber in a field by means of 30 KeV electron probe. The acquisition time was fixed at 50 sec.

In order to identify the mineralogical variety of asbestos, the key element ratios (Si: Mg in case of chrysotile and Si: Al or Si: Fe for amphiboles) were taken into account for samples and standards.

Results and discussion

The infrared spectra for UICC standards compared with spectra of airborne collected samples showed the presence of chrysotile asbestos in all airborne collected samples. These spectra contained six main vibrational bands (fig.1), in a good agreement with the literature data [4].

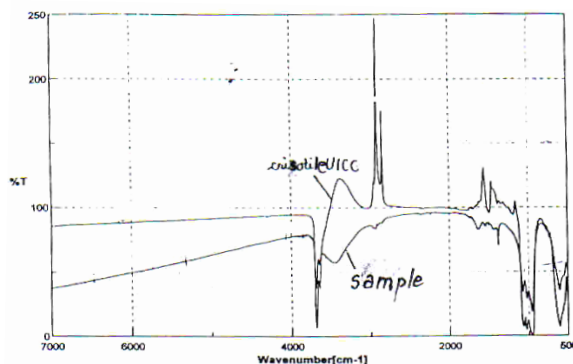


Fig. 1 FT-IR spectrum of a sample collected in the workplace area in the technological process of manufacturing of the insulation elements in comparison with the spectrum of UICC standard chrysotile asbestos

The results of SEM morphological analyze showed the presence of curved fiber in all asbestos samples collected from the working area as well as in UICC chrysotile standard. Chemical elemental composition analyze was performed on three fiber of each analyzed sample. EDXS spectra of all airborne samples showed the presence of Mg and this indicates the chrysotile asbestos presence (fig.2).

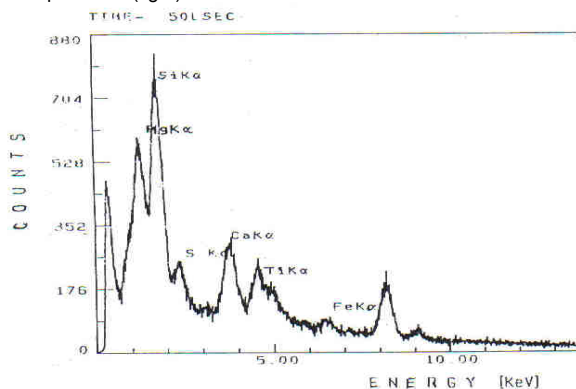


Fig. 2. EDXS spectrum of a fiber in a sample collected in the working area in the technological process of manufacturing of the insulation elements

The quantitative elemental analysis showed that the Si:Mg ratio is 1 for all the airborne samples as well as UICC chrysotile asbestos, showing the presence of chrysotile asbestos in all investigated samples.

Conclusions

We can conclude that both physico-chemical methods used in this paper identified the presence of chrysotile and this could be used as criteria to define the analytical performances of these methods, in spite of the differences in their analytical principles. The two methods are less time consuming.

We have to take into account the high price of the technical instrumentation, which could be a problem in the routine airborne asbestos monitoring in the occupational environment.

[1] D. Balducci, F. Valerio, Intern. J. Environ. Anal. Chem., 77, 315-318 (1986)

[2] L. Rodrique, Revue des Question Scientifiques, 155 (2), 225-228 (1984)

[3] AIA Health and Safety Publication. Recommended Technical Method no. 2 (RTM2). Method for the determination of airborne asbestos fiber and other inorganic fiber by scanning electron microscopy (1984)

[4] H. Suquet, Clays and Clay Minerals, 37, 439-443 (1989)

THE NECESSITY OF SEM ANALYSIS IN OUTDOOR ENVIRONMENT MONITORING OF AIRBORNE ASBESTOS FIBRES

L. Bologna, A. Ferri, E. Lauria, M. Wojtowicz

Polo amianto, ARPA Piemonte, Grugliasco (TO), Italy

Le modalità di controllo dell'amianto negli ambienti di lavoro sono definite da anni, sia con provvedimenti a livello nazionale, sia con normative dell'UE ed, in genere, internazionali.

Con la dismissione dell'utilizzo dell'amianto per scopi produttivi, rimangono da considerarsi "ambienti di lavoro" quelli legati alla bonifica in genere, ai lavori di manutenzione delle strutture con amianto, al trasferimento in discarica, al trattamento dei rifiuti, all'estrazione di pietrisco da cave inquinate da minerali d'amianto, a cantieri stradali o edili in presenza di affioramenti naturali.

La normativa vigente si applica a "tutte le attività lavorative nelle quali vi è rischio di esposizione alla polvere proveniente dall'amianto" (art. 22 D.Lgs. 277/91) e, riferendosi alla tutela dei lavoratori, non considera la particolarità di alcune delle situazioni sopra citate. Inoltre, non esiste attualmente una norma di riferimento che prenda in considerazione l'inquinamento negli ambienti di vita, con indicazioni specifiche per valutare il rischio di esposizione che può derivare dall'amianto antropico o naturale. In presenza di cantieri non confinati, ad esempio, si verificano molte situazioni che possono comportare esposizioni di tipo non professionale. Nasce quindi l'esigenza di adottare nuovi o più corretti procedimenti, in termini di campionamento e analisi, in particolar modo per quanto riguarda i monitoraggi in ambienti esterni.

In riferimento alle tecniche d'analisi, ad esempio, risulta evidente che l'indicazione del D.Lgs. 277/91, secondo cui tutte le fibre "regolamentate" (definite nell'art. 30, comma 3), lette in MOCF, sono da considerarsi amianto, in fase di controllo dell'esposizione dei lavoratori, non è opportuna in ambienti esterni, per di più in assenza di attività produttive coinvolgenti l'amianto come materia prima, in quanto può portare a grossi errori di valutazione, sia per i controlli personali, sia d'area (interni ed esterni al cantiere). Questo per la compresenza di diverse fibre, organiche ed inorganiche, presenti in natura, fra cui è difficile discriminare, applicando solo criteri morfologici, per cui non è attendibile approssimare il numero delle fibre totali a quello delle fibre d'amianto.

Nel caso di cantieri che comportino la lavorazione di materiali rocciosi, inoltre, si originano svariati tipi di schegge, che, se di dimensioni regolamentate, devono essere conteggiate in MOCF.

L'utilizzo della microscopia elettronica risolve quasi del tutto l'incertezza legata all'identificazione delle fibre, fornendo indicazioni più realistiche sull'effettiva esposizione ad amianto dei soggetti coinvolti.

In caso però di indagini ambientali più estese, la sola applicazione della metodica in SEM non sarebbe opportuna, dal momento che monitoraggi significativi comportano inevitabilmente campionamenti numerosi, ripetuti ed effettuati in condizioni meteo-climatiche differenti, insieme alla necessità di contenere tempi e costi d'analisi. È necessario, quindi, trovare un compromesso, per ottenere dati utili senza diminuire il livello di conoscenza.

Nella presente memoria si propongono alcune fra le esperienze degli autori relative a cinque indagini effettuate, per motivi diversi, in ambienti esterni, e precisamente: la prima, del 1990-'91, è relativa al monitoraggio nei pressi di una cava contaminata da tremolite, nel comune di Trana (TO); altre due si riferiscono ad indagini effettuate, tra il 1994 e il 1995, per valutare l'inquinamento all'esterno di stabilimenti produttivi di cemento amianto, a Szczucin (Polonia), presso lo stabilimento Eternit e a Cerdanyola (Spagna) nei dintorni dello stabilimento "Uralita"; una quarta indagine, avvenuta tra il 1999 e il 2002, è riferita al monitoraggio della città di Casale M.to (AL), maggior sito produttivo per il cemento-amianto in Italia e attuale sito d'interesse nazionale per le bonifiche; la quinta indagine, attualmente in corso, è quella relativa al controllo del risanamento ambientale del sito di Balangero, ex miniera d'amianto più grande d'Europa.

In generale le attività di monitoraggio sono state condotte secondo i seguenti criteri: sopralluogo preliminare per l'esame delle peculiarità dell'area e programmazione dell'indagine; realizzazione delle campagne di prelievo; analisi in MOCF della totalità delle membrane; analisi in SEM di una percentuale di campioni variabile dal 20 al 40% a seconda dei risultati ottenuti in MOCF (scegliendo le membrane più "cariche" di fibre definite "asbestosimili")² e della situazione in esame.

L'indagine svolta nel comune di Trana ha successivamente determinato la cessazione dei lavori nella cava in questione, dal momento che, con l'attività estrattiva in corso, le concentrazioni di fibre di tremolite rilevate in SEM risultavano, in media, pari a 47 ff/l in ambienti di vita, con picchi superiori a 100 ff/l. Tra i 64 campioni, prelevati a diversa distanza dalla cava e durante fasi lavorative di diversa entità, i valori più alti sono stati riscontrati nella postazione della scuola elementare, circondata da strade ricoperte da materiale di cava. Si può presumere che l'aerodispersione delle fibre fosse dovuta al traffico veicolare. Dal punto di vista analitico si è riscontrata una buona corrispondenza fra i risultati in MOCF relativi alle fibre asbestosimili e quelli in SEM riferiti alle fibre d'amianto. Questo perché le fibre di tremolite sono assai diverse dalle fibre organiche, e ciò ha permesso di non considerare quest'ultime nel conteggio in MOCF.

Per quanto riguarda le esperienze di monitoraggio nei pressi di stabilimenti produttivi, i risultati ottenuti sono fortemente legati alla distanza di prelievo, per cui in Spagna, sono stati riscontrati valori bassi principalmente perché le autorità locali non hanno ritenuto opportuno avvicinarsi a meno di cento metri dallo stabilimento. In base alle informazioni ottenute all'epoca dell'indagine, all'interno dello stabilimento Uralita si utilizzava solo crisotilo. Le concentrazioni d'amianto riscontrate in SEM sono al di sotto di 1 fibra/litro. Le concentrazioni di fibre totali in MOCF risultano in media pari a 2 ff/l (calcolate su 56 campioni).

La campagna di prelievi in Polonia ha compreso un totale di 96 campioni, quattro postazioni, con tre campionamenti/giorno per postazione. Il valore in fibre d'amianto più elevato trovato in SEM è stato di 6,2 ff/l (di cui 4,4

² Fibre che hanno le caratteristiche ottiche e morfologiche degli amianti, nei limiti delle possibilità di lettura del microscopio ottico.

di crocidolite), in corrispondenza della discarica dello stabilimento. Si evidenzia il fatto che la crocidolite non era più utilizzata da almeno 5 anni nel ciclo produttivo, ma veniva ancora aerodispersa durante la movimentazione dei rifiuti.

L'indagine ambientale effettuata sul territorio di Casale M.to ha avuto una durata di tre anni, con un totale di 1192 campioni, su 14 postazioni. I punti di prelievo attorno allo stabilimento Eternit, all'epoca in fase di bonifica, sono stati quelli maggiormente indagati, attraverso analisi con entrambe le tecniche microscopiche. Il valore massimo di concentrazione in fibre d'amianto, nei tre anni, è stato di 6,1 ff/l, relativo ad una postazione prossima agli estrattori del cantiere di bonifica dello stabilimento Eternit. In quell'occasione, il dato in fibre totali in microscopia ottica era risultato minore in quanto erano presenti fibre con diametro inferiore a 0,2 micron, non visibili a 500 ingrandimenti.

Il monitoraggio in ambiente esterno presso l'ex miniera di Balangero, nel corso del risanamento ambientale del sito, pone ancor più in evidenza la necessità di utilizzare la microscopia elettronica. Nel caso specifico sono state rilevate fibre "ultrasottili", non visibili nemmeno nelle condizioni standard di lettura in SEM (2000 ingrandimenti). A causa dello spostamento di pietrisco contenente crisotilo, necessario alla sistemazione idrogeologica del versante lato Corio (discarica materiale di cava), infatti, si disperdono nell'aria fibre con diametri inferiori a 0,1 micron, visibili soltanto ad ingrandimenti superiori a 2000. Nelle microfotografie sottostanti, sono rappresentate alcune fibre del tipo descritto, individuate effettuando la lettura dei filtri a 4000 ingrandimenti.

Alcuni dati, emblematici per il confronto fra le due tecniche microscopiche, sono stati riscontrati in prossimità delle aree di movimentazione del pietrisco e in condizioni di forte vento. I valori di concentrazione ottenuti mostrano una differenza di uno o due ordini di grandezza fra le fibre d'amianto conteggiate in SEM e quelle osservate in MOCF. In microscopia elettronica si sono trovati valori intorno a 100 ff/l, con un picco superiore a 500 ff/l; con la microscopia ottica, non si sono superate le 35 ff/l, anche in corrispondenza del picco di concentrazione massimo riscontrato in SEM.

In corrispondenza dei punti di prelievo situati presso il centro abitato, i valori di concentrazione in fibre d'amianto in SEM rimangono al di sotto di 1 ff/l e l'osservazione di fibre "ultrasottili" rappresenta un'eccezione. Si può ipotizzare che ciò sia dovuto alle proprietà aerodinamiche delle fibre di crisotilo, caratterizzate da una minore tendenza a diffondersi nell'aria rispetto a quelle di tremolite.

È bene ricordare che la concentrazione delle fibre aerodisperse varia notevolmente in rapporto alle condizioni climatiche e alla presenza di fonti inquinanti in prossimità dei punti di prelievo. A prescindere dalla tecnica microscopica impiegata per l'analisi, è necessario effettuare un'indagine estesa, prelevando campioni in condizioni climatiche differenti oppure in concomitanza di quelle che favoriscono la dispersione delle fibre (clima secco, correnti d'aria, ecc.). In ogni caso, è essenziale fornire un'interpretazione dei risultati per correlare il dato ottenuto alle condizioni al contorno, considerata, anche, la natura indiretta della misura, affetta dall'incertezza che caratterizza i metodi di conteggio.

In generale si è verificato che in assenza di attività lavorativa, dovendo effettuare un monitoraggio ambientale, quindi per un periodo sufficientemente lungo, conviene utilizzare la microscopia ottica come metodo di analisi rapido, più economico e in grado di fornire una prima indicazione sulle aree "a rischio". Successivamente, su di un'aliquota dei campioni, scelti fra quelli ritenuti più "carichi", è opportuno compiere una verifica in microscopia elettronica, per meglio caratterizzare le fibre osservate, a causa della compresenza di svariate tipologie. L'associazione delle due tecniche permette quindi di avere risultati attendibili in tempi relativamente brevi. L'ordine di grandezza delle concentrazioni non sempre consente di effettuare un paragone diretto fra i risultati ottenuti con le due tecniche microscopiche, tuttavia aggiunge dati in favore della tesi secondo cui il rapporto fra le fibre totali in MOCF e le fibre d'amianto in SEM non solo non è di 10:1 (come indicato nel D.M. 06/9/94), ma non è neppure costante.

In presenza di lavori che comportino la movimentazione di materiale con amianto, come attività di scavo nei pressi di affioramenti naturali, risulta evidente la necessità di utilizzare la microscopia elettronica in quanto le dimensioni delle fibre liberate nell'aria possono risultare assai più fini, per l'azione meccanica disagregante a cui sono sottoposte.

Un fattore da non trascurare nella scelta della tecnica analitica da utilizzare è la destinazione dei risultati, ovvero a chi viene comunicata l'informazione finale sulla qualità dell'aria prelevata. Considerato che non è nota la soglia di rischio, l'utente medio, estraneo alle problematiche tecniche finora discusse, sarà interessato comunque ad un valore di concentrazione in fibre d'amianto e non potrà essere soddisfatto da un dato in termini di fibre totali, ottenibile in MOCF.

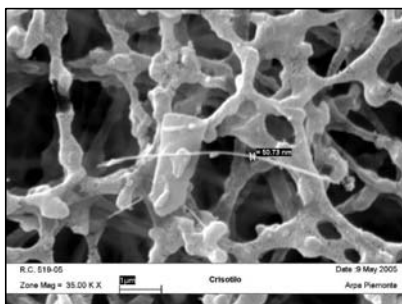


Figura 1 - Esempio di fibre "ultrasottili". Il diametro indicato è pari a 0,06 micron. Ingrandimento a 35000X.

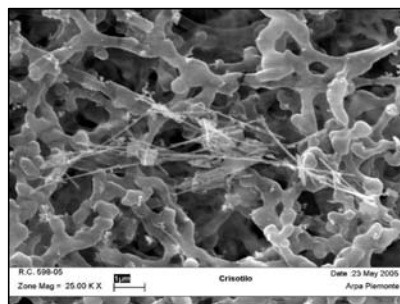


Figura 2 - Esempio di fibre "ultrasottili" in fascio disagregato. Ingrandimento a 25000X.

MONITORING OF AIRBORNE FIBRES DURING REMEDIATION OF THE ABANDONED ASBESTOS MINES OF BALANGERO AND CORIO

M. Bergamini (1), A.Ghione (1), B.Fubini (2)

(1) R.S.A. S.r.l. Società a capitale pubblico per il risanamento e lo sviluppo ambientale dell'ex-amiantifera di Balangero e Corio

(2) Centro interdipartimentale dell'Università di Torino "G.Scansetti" per lo studio degli amianti e di altri particolati nocivi

Nell'ambito delle attività di risanamento ambientale dell'ex miniera di amianto più grande d'Europa, sito di bonifica di interesse nazionale (Legge 09.12.1998, n.426), è prevista l'esecuzione di considerevoli opere di ingegneria naturalistica per la sistemazione idrogeologica delle vasche di decantazione dei fanghi contenenti amianto e delle discariche di materiale lapideo in giacitura di versante.

La messa in sicurezza del c.d. Rio Pramollo prevede il confinamento di c.a. 15.000 metri cubi di fanghi contenenti amianto al 30% e, in particolare, i lavori sulla discarica lapidea c.d. Fandaglia, interessano un volume di pietrisco con amianto stimato in c.a. 30 milioni di metri cubi con superficie esposta superiore a 60 ettari.

In sede di approvazione del Progetto Definitivo delle opere, in data 06.04.2001, la Conferenza dei Servizi, convocata presso il Ministero dell'Ambiente, ha disposto che venisse elaborato: "...da parte di RSA,...un Piano di monitoraggio ambientale, puntuale e continuo, delle fibre di amianto durante le varie fasi degli interventi con speciale riferimento all'aerodispersione, da sottoporre a CRA-ARPA Piemonte...", la quale, nell'ambito di apposita Convenzione (10.02.2005), provvede alla validazione delle procedure di campionamento e analisi.

Il Piano di Monitoraggio prevede oltre 2.000 campionamenti all'anno, a partire dal 2004, con analisi in microscopia ottica (MOCF) e, per una parte, in microscopia elettronica (SEM).

Salvo le analisi di controllo, eseguite da A.R.P.A.- Polo Amianto, il complesso delle analisi è stato eseguito presso il Laboratorio Analisi di R.S.A. S.r.l., attrezzato per la Microscopia Ottica in Contrasto di Fase (D.M. 06.09.1994; D.M. 14.05.1996), allestito appositamente in sito al fine di operare con tempestività nel prelievo e nelle analisi MOCF verificando nel minor tempo possibile l'insorgenza di eventuali situazioni di allarme.

Con riferimento al D.M. 06/09/1994 i criteri di conteggio per la microscopia ottica in contrasto di fase (stabiliti con Dir. CEE 83/477) impongono di considerare qualunque particella di forma allungata avente *lunghezza* > 5 µm, *diametro* < 3 µm e rapporto *lunghezza/diametro* > 3:1; tuttavia in molti casi è stato possibile distinguere, sulla base di caratteristiche morfologiche, specifiche particelle allungate non di amianto; sono state perciò riportate nei Rapporti di Prova, per ciascun filtro, sia il numero di fibre totali conteggiate, sia il numero di fibre asbestosimili che sono oggetto delle rielaborazioni eseguite.

Il monitoraggio è riferito alle lavorazioni di cantiere, alla rete viaria e al bacino di cava mineraria individuati all'interno dell'area perimetrata di bonifica (D.M. Ambiente 10.01.2000), nonché agli abitati limitrofi.

Non essendo prevista dalla vigente normativa una soglia di riferimento per l'esposizione ad amianto negli ambienti di vita si è ritenuto di formulare, in via preliminare soggetta ad opportune modifiche in corso di esecuzione dei lavori, un sistema di limiti in base al cui superamento si definisce la sussistenza di una situazione di allarme (Regione Piemonte, Direzione tutela e risanamento ambientale, prot.317/22 del 12.01.2004):

"...nell'area di cantiere non dovrà essere superata la concentrazione di 50 ff/l misurate in M.O.C.F. (riferimento desunto dall'Allegato normativo al D.M. 06.09.1994 art. 5 comma 1);

nelle aree di abitato non dovrà essere superato il doppio della concentrazione media misurata in M.O.C.F. da ARPA Piemonte nel corso delle campagne di monitoraggio eseguite a partire dalla chiusura dell'attività mineraria; tale limite non potrà in ogni caso superare la concentrazione massima di 20 ff/l misurate in M.O.C.F. ritenuto, in via approssimativa ed in base alla normativa tecnica di settore, equivalente al limite di restituibilità per ambienti bonificati di 2 ff/l di amianto misurate in S.E.M."

Negli abitati di Balangero, Corio, e della frazione Cudine di Corio, durante il periodo compreso tra maggio 2004 e aprile 2005, su circa 250 dati per ogni punto di monitoraggio, si sono registrati valori inferiori a 1,00 ff/l nel 98% dei casi e, in un solo caso, il dato di concentrazione calcolato sulle fibre asbestosimili ha superato le 2 ff/l.

Per l'area di cantiere sono stati presi in considerazione 532 dati rilevati alla sommità della Discarica Fandaglia, sul lato di Corio, nello stesso periodo compreso tra maggio 2004 e aprile 2005, coincidente con il maggior sviluppo degli scavi, delle lavorazioni di scarico mediante teleferica e della successiva movimentazione dei materiali costituenti la discarica lapidea.

Con esclusione dei valori di picco, considerati a parte, il massimo valore registrato è pari a 18,85 ff/l e la media risulta pari a 0,79 ff/l; il 99% dei valori di concentrazione risulta essere inferiore a 6,00 ff/l asbestosimili.

Considerando separatamente i valori di picco sulle fibre aerodisperse si rileva che questi vengono a coincidere con le condizioni climatiche più avverse a causa del vento, indipendentemente dalle lavorazioni di cantiere che, in occasione di vento teso, vengono sospese.

In particolare, sono stati sottoposti ad analisi in microscopia elettronica (SEM) di ARPA- Polo Amianto i filtri prelevati in occasione di giornate con vento di *phon* che può raggiungere, in alcuni casi, velocità superiori a 120 km/h (Monte San Vittore, 21.01.2005).

I risultati delle analisi ARPA, eseguite al SEM a 4.000 ingrandimenti, ovvero in condizioni di maggior definizione rispetto a quanto previsto al D.M. 06/09/1994 (2.000 x), mettono in evidenza un particolare carattere delle fibre di crisotilo esaminate, risultate in netta prevalenza con diametro inferiore a 0,2 micron, al di sotto del limite di risoluzione dell'osservazione in microscopia ottica (MOCF).

Mettendo a confronto i risultati delle analisi MOCF eseguite da R.S.A. S.r.l. e i risultati delle analisi SEM eseguite da ARPA- Polo amianto, si è compilata una tabella dei valori massimi registrati in condizioni di vento, da debole a forte, con una valutazione del rapporto tra le concentrazioni di ff/l totali in MOCF e ff/l di amianto in SEM:

RSA F.to	Data	Luogo campionamento	RSA MOCF ff/l tot.	RSA MOCF ff/l asb.	ARPA SEM ff/l tot.	ARPA SEM ff/l amianto	Rapporto MOCF/SEM
01179	24/09/2004	Discarica versante Corio gradoni sommitali - scarico	2,56	1,44	<0,55	<0,55	nessuna fibra rilevata
01176	24/09/2004	Discarica versante Corio teleferica scarico	4,47	2,72	10,14	10,14	c.a 1:2
01177	24/09/2004	Discarica versante Corio passi d'uomo	2,24	0,48	1,10	1,10	c.a 2:1
01584	19/11/2004	Discarica versante Corio gradoni sommitali - carico	51,35	34,74	584,49	579,01	c.a 1:11
01585	19/11/2004	Discarica versante Corio gradoni sommitali - scarico	36,34	24,04	97,96	97,23	c.a 1:3
01576	19/11/2004	Cudine frazione di Corio	2,40	1,28	3,84	2,19	c.a 1:1
01575	19/11/2004	Balangero Centro abitato	1,92	0,64	1,65	<0,55	nessuna fibra rilevata
01893	21/01/2005	Discarica versante Corio teleferica scarico	11,74	9,66	94,27	94,00	c.a 1:8
01891	21/01/2005	Cudine frazione di Corio	6,87	5,91	0,28	<0,28	nessuna fibra rilevata
01938	27/01/2005	Discarica versante Corio gradoni sommitali - carico	0,64	0,32	0,28	<0,28	nessuna fibra rilevata

Il confronto tra i dati consente di ritenere, in via preliminare, che vi sia correlazione tra i risultati dell'analisi MOCF e i corrispondenti risultati dell'analisi al SEM, ma con ordini di grandezza numerici in rapporto evidentemente non coerente con le indicazioni di cui al D.M.06.09.1994 (20 ff/l MOCF = 2 ff/l SEM).

Per quanto i dati esposti siano da considerare come valori anomali nell'arco di un intero anno di prelievi eseguiti giornalmente, con esclusione dei soli giorni festivi, la problematica che emerge impone un diverso approccio analitico volto all'individuazione del dato significativo, sia per quanto concerne gli ambienti di vita, sia per quanto riguarda l'esposizione dei lavoratori.

Pur confermandosi la validità di analisi MOCF, secondo le indicazioni del D.M.06.09.1994, ai fini di un celere riscontro sul monitoraggio ambientale, devono essere necessariamente indagate le situazioni di maggior criticità mediante una attenta analisi in SEM.

Si è provveduto quindi ad adeguare le attrezzature di prelievo, le modalità di campionamento e di analisi alle nuove necessità evidenziate: negli ambienti di vita i campionamenti vengono eseguiti su filtri con \varnothing 45 mm e volume d'aria prelevato pari a 3000 lt., con flusso di campionamento di c.a 10 litri/min. per un tempo di c.a 5 ore, in modo da intercettare la presenza delle polveri fini aerodisperse.

Nel confronto parallelo con le modalità di campionamento su filtri con \varnothing 25 mm e volume d'aria prelevato pari a 540 lt., con flusso di campionamento di 4,5 litri/min. per un tempo di 2 ore, più adeguate per le zone di lavoro, il campionamento su di un tempo prolungato, per i centri abitati, si rivela maggiormente cautelativo nel 70 % dei valori calcolati su 46 filtri esaminati.

Sono stati inoltre installati campionatori sequenziali in grado di rilevare automaticamente, in occasione di condizioni meteorologiche ritenute significative, l'intero arco delle 24 ore, in modo da ricercare eventuali indicazioni sul *fall out* delle polveri aerodisperse.

Nell'ambito della Convenzione A.R.P.A. Piemonte - R.S.A. Srl sono state intensificate nel breve periodo le analisi in microscopia elettronica (SEM), anche sottoponendo a controanalisi i dati in microscopia ottica (MOCF) di esposizione dei lavoratori, in modo da verificare l'effettivo livello di esposizione personale, manifestando con ciò un limite insito nelle prescrizioni di cui all'Allegato V del D.Lgs. 15.08.1991 n.277, peraltro non risolto nella Direttiva 2003/18/CE.

In base ai riscontri riportati su parere del Centro "G.Scansetti" (luglio 2005), sui campioni di pietrisco prelevati sulla discarica Fandaglia, non risulta che le operazioni di scavo e rimodellamento delle superfici abbiano comportato un significativo aumento nel rilascio di fibrille di amianto; più realisticamente ne è emersa la presenza in quanto sono state ricercate con adeguata strumentazione analitica su campioni prelevati nelle più avverse condizioni.

Ciò conferma la validità del rapporto convenzionato tra l'Impresa e l'Ente di controllo, poiché è risultato possibile ricercare le condizioni di maggior criticità su una popolazione di oltre 2.500 campioni disponibili.

Un riconoscimento particolare ai dipendenti di R.S.A. S.r.l.: G. Marangoni, M.G. Luiso, A. Demaria e R. Pasquali che, con il loro quotidiano lavoro, hanno reso possibile questa sintesi di dati.

DIMENSIONAL MICROSCOPIC ANALYSIS OF ASBESTOS BUNDLES RELEASED INTO ATMOSPHERE FROM AN ASBESTOS-CEMENT ROOF

A. Cattaneo¹, V. Foà¹, G. Chiappino¹

¹Occupational Health Department, Università degli Studi di Milano, Italy

This study was conducted in an industrial location including a building covered by a 2500 m² ACM (asbestos-cement roof). The atmospheric settling dust sampling was performed for 26 days with a method first proposed by Chiappino et al. in 1999 [1]. This method captures dust by microscopic slides covered with an appropriate adhesive film. The sampling instruments were arranged, in groups of three, in five different positions from the asbestos-cement source (Table 1), in order to define possible morphological differences between amphiboles and chrysotile, as well as qualitatively evaluate the mass influence on the sedimentation process. The analysis was carried out in phase contrast optical microscopy, using the dispersion staining method, to facilitate qualitative discrimination of asbestos minerals.

Table 1 – Average length, diameter and aspect ratio of asbestos, collected in 5 different positions from ACM source.

POSITION [horizontal - vertical distance] (m)	AMPHIBOLES			CHRYSTOTILE		
	L (μm)	D (μm)	L/D	L (μm)	D (μm)	L/D
1 [0,3-0]	472,95	6,84	69,14	981,04	81,03	12,11
2 [0,75-5]	401,83	5,89	68,22	767,81	43,37	17,70
3 [5-6]	690,50	11,80	58,52	487,50	40,21	12,12
4 [28-6]	298,33	28,17	10,64	407,14	57,86	7,04
5 [7-0]	371,82	5,00	74,36	330,83	33,09	10,00
Average	461,87	7,38	62,67	638,78	50,85	12,56

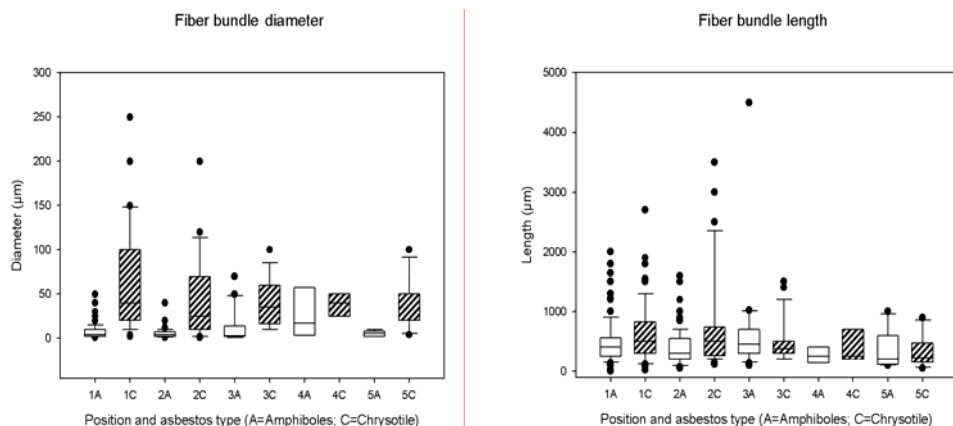


Figure 1 – Box plots showing the size distribution (in length and diameter) of asbestos bundles collected in 5 different positions from ACM source. Amphiboles (A): white boxes; Chrysotile (C): filled boxes.

The analysis of the collected data, summarized in Table 1 and Figure 1, allowed to conclude that the average diameter of the released chrysotile bundles is higher than amphibole bundles. Consequently, since length variation is lower, the amphibolic asbestos bundles show aspect ratios higher than chrysotile bundles. The chrysotile dimensions show an inversely proportional increase to asbestos source distance, since they have higher diameters than amphiboles and consequently a greater mass. This fact justifies the preferential sedimentation of chrysotile bundles in the immediate proximity of the asbestos-cement roof in spite of their lower density as compared with amphiboles.

[1] G. Chiappino, V. Giannelle, A. Todaro, O. Picchi, Med. Lav., 3, 519-26 (1999)

SPECIFIC ANALYTICAL TECHNIQUES FOR ASBESTOS ANALYSIS IN AIR: COMPARISONS AND EVALUATIONS

G. Cecchetti

Faculty of Environmental Sciences, Università degli Studi "Carlo Bo", Urbino, Italy

The study of asbestos in air has always met with considerable difficulties, especially when it comes to evaluating the number of airborne fibers, as the subjectivity of the single operator has always entailed a degree of uncertainty in the field of microscopy. Such uncertainty has become even more evident with the progressive reduction of exposure limits.

This study aims at comparing and evaluating different methods. Four techniques are considered: phase contrast light microscopy, scanning and transmission electron microscopy and finally x-ray diffractometry. This last technique was used when it was possible to evaluate airborne weight concentration so as to immediately assess the presence of asbestos dust and evaluate its weight percentage. These data, although scarcely meaningful from a health point of view, allowed the evaluation of pollution in several work places before assessing the actual exposure by counting the exact number of fibers.

Light microscopy techniques have always been more frequently used in work places because they were easy to carry out and also because in work places it was possible to find almost exclusively asbestos fibers, especially in those environments where asbestos was used as raw material. Today this situation is found in abatement activities. When using light microscopy it can be difficult to tell the different fibers apart. This difficulty has been overcome by applying a restrictive evaluation method, that is all fibers counted were considered asbestos fibers.

On the other hand, in every day life environments, the concurrent presence of different kinds of fibers required the use of more sophisticated analysis techniques, such as scanning electron microscopy and the use of energy dispersive x-ray scanners which made it possible to identify the nature of the fibers on the basis of their chemical composition. In some of the cases, transmission electron microscopy was very useful to identify those fibers that were more difficult to tell apart because thanks to this technique it is possible to perform a wavelength dispersive x-ray analysis.

Session: Analysis in soils and bulk materials

B. Tylee	Quality of analyses of asbestos in soil
P. Di Pietro	A new method for the measurements of low fibre levels in soils with XRD and FTIR
S. Shutler	Sampling materials and fibre identification by polarised light optical microscopy (HSE test method MDHS77)
E. Lauria	Methodological approach to the analysis of asbestos in rocks
C. Cazzola	Methods and applications for quantitative analysis of asbestos in rocks and soils by light optical microscopy
C. Groppo	Quantitative analysis of fibrous minerals in rock samples using BSE images and micro-raman spectroscopy
C. Rinaudo	Raman spectroscopy: a rapid technique to identify asbestos phases

QUALITY OF ANALYSES OF ASBESTOS IN SOIL

B. Tylee

Health and Safety Laboratory, Harpur Hill, Buxton, SK17 9JN, UK

Many countries have the problem of dealing with asbestos contamination of land, arising from past industrial use. The contamination levels at which residential and commercial use is considered 'safe', are still being developed in Europe. Also determinations are often needed for the removal and disposal of asbestos contaminated waste. The analyses of asbestos in soils is generally carried out using polarised light or electron microscopy. However these determinations are much more difficult than the analysis of asbestos in propriety materials, where the concentration of asbestos is usually greater than 3%. The starting point for any soil survey is to obtain a meaningful and representative sub-sample for further analysis. Contamination of asbestos in soil can fall into two types; (i) fragments of intact asbestos containing materials (ACMs) and (ii) loose fibres that were never incorporated into an ACM or have been produced by the break up of friable ones.

These samples often need extra preparation to remove water/oil etc, which would interfere with the analyses and lead to false negatives. The limit of detection and limit of quantification of the analytical techniques is often not known and may result in an inappropriate analysis being applied. A greater number of other fibres may be present (compared with ACMs) as well as mineral fragments that can be mistaken for asbestos, leading to false positives being reported. Also there is a lack of suitable laboratory reference material and appropriate quality control material for this technique. In our experience the analyst may have little experience of the above problems or may have been allowed too little time to overcome some of the difficulties that are presented.

The Asbestos In Materials programme provides asbestos samples and performance scores (4 samples of 3 rounds per year) to 260 laboratories throughout Europe. When the scheme started in 1996, the analytical quality of many of the laboratories was poor (as has been found with other proficiency testing schemes) with up to 30% of laboratories producing incorrect results for some ACMs. This has dramatically improved over the years. Since 1998 we have also introduced a number of samples, representing contaminated soils, for both qualitative and quantitative analysis to test the analytical performance of laboratories. Also in 2004 a special round was carried out where the samples had both heterogeneous and homogeneous asbestos components.

The results of these proficiency tests will be discussed and compared with typical performances for propriety materials. Recommendations will be made for the improvement of these techniques, particularly the incorporation of more realistic samples into PT programmes, that simulate some of the difficulties and challenges that occur in contaminated land surveys. Incorrect analyses of contaminated land are not just a waste of money to the client, they can present a lasting, and expensive health problem for the future.

A NEW METHOD FOR THE DETECTION OF LOW LEVELS OF FREE FIBRES OF CHRYSOTILE IN CONTAMINATED SOILS BY X-RAY DIFFRACTION (XRD) AND INFRARED SPECTROSCOPY (FTIR)

I. G. Lesci^a, E. Foresti^a, A. F. Gualtieri^b and N. Roveri^a. P. Di Pietro^c, M. Campanella^c M. Marcozzi Rozzi^c

a Laboratorio di strutturistica chimica ambientale e biologica Dipartimento di Chimica "G. Ciamician", Alma Mater Studiorum, Università di Bologna Via Selmi 2, 40126 Bologna, Italy. E-mail:norberto.roveri@unibo.it; Fax: +39 051 2099456; Tel: +39 051 2099486

b Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, Via S. Eufemia 19, 41100 Modena, Italy.

c A.R.T.A. Agenzia Regionale per la Tutela dell'Ambiente, Dip. Provinciale di Teramo, Centro Regionale di Riferimento per l'Amianto (C.R.R.A.), P.zza Martiri Pennesi 29, 64100 Teramo, Italy. E-mail:p.dipietro@artaabruzzo.it, Fax: +39 0861 2565528; Tel. +39 0861 2565545

The health hazards associated with free asbestos fibres in soils led to severe regulations which now apply in most western countries. Italian law (D. M. 471/1999) establishes that the asbestos concentration must not exceed 1 g of free fibres per kg of dry soil. The detection limit of 0.1 wt% is reached by XRD and FTIR analysis with an enrichment of free fibres of chrysotile in the sample using a standard laboratory elutriator for sedimentation analysis by an improvement of a method just reported by the same authors.^[1]

The detection limit obtained using stoichiometric synthetic chrysotile microfibers mixed in different soil is at or below the 0.05 wt% level as a function of the soil typology. The linearity of the XRD and FTIR obtained plots reveals that the procedure can be successfully applied to soil samples of different typology (calcareous, clayey, sandy and sandy-organic) through the removal of eventual interferences due to some matrix components.

The addition of NaCl and surfactant solution allows regulation of the ionic strength and the particle aggregation, respectively

The results show that the enrichment treatment in an elutriator can be satisfactorily applied to determine very low chrysotile content in the soil in order to quantify the asbestos pollution. XRD and FTIR analysis carried out on conventional instruments allow determination of the amount of chrysotile-ree fibres below 1 wt% in enriched samples. The procedure can be successfully applied to several kinds of soils and it does not need any special technique. This new

analytical method replies to the request of several public institutions and private companies for an appropriate quantitative determination of free fibres of chrysotile in contaminated grounds.

[1] E. Foresti, M. Gazzano, A.F. Gualtieri, I.G. Lesci, B. Lunelli, G. Pecchini, E. Renna and N. Roveri; *Anal. Bioanal. Chem.* 2003 376, 653-658.

SAMPLING MATERIALS AND FIBRE IDENTIFICATION BY POLARISED LIGHT OPTICAL MICROSCOPY (HSE TEST METHOD MDHS 77)

S. Shutler

*Commercial Manager ALcontrol Shutler
Newcastle under Lyme, United Kingdom*

Polarised light/dispersion staining optical microscopy is the method most commonly used in the United Kingdom to identify the presence & type of asbestos fibres in bulk materials. The method was originally described in HSE Test Method MDHS 77 and has recently been re-issued with minor amendments ⁽¹⁾.

The method consists of two distinct parts. Firstly the material, which is suspected to contain asbestos, is examined by use of a low power stereo microscope. Fibres observed are given a tentative identification based upon morphology and physical characteristics. The second phase of the procedure is to mount a small number of the observed fibres in a refractive index liquid, which is chosen to match the refractive index RI for the tentatively identified asbestos variety. The fibres are then examined by polarised light optical microscopy, and if the correct RI liquid was chosen, will exhibit known effects. Should this not occur then the process is repeated using the next most likely fluid until a positive identification can be made.

Sample treatment may be required to release fibres from the body of the sample and to remove adhering particulate matter, which could obscure optical effects. The simplest treatment involves mechanically breaking the sample to reveal clean edges from which fibres may then be visible. Calcium carbonate & calcium silicate may be removed with dilute acids. Organic binders can be removed with solvents or by ignition. Wet samples require drying before initial examination or fibres may not be visible.

Laboratory requirements are relatively inexpensive. A suitable fume cabinet with a minimum face velocity of 0.5m/s and a high efficiency (HEPA) filter is necessary when samples are examined, and a suitable stereo microscope having a typical magnification of x8 to x40. A polarised light microscope with Köhler (or Köhler type) illumination is needed for the second stage of the analytical procedure. This instrument needs various accessories including a removable analyser, a removable first order red compensator and a dispersion staining objective with a central stop in its back focal plane. In addition to reagents for sample treatment, a minimum of five high dispersion liquids are required to achieve a positive match with the different asbestos types.

While the method has wide application for solid materials, there are limitations when fibres have widths below one micron. Additionally it may not be possible to distinguish between tremolite and anthophyllite and tremolite and actinolite. The quoted sensitivity is that one fibre may be found in a few milligrammes of dispersed material. For a fibre of 100 microns length and 2 microns width this implies a detection limit in the order of 1 part per million by mass.

Identification requires significant operator training & experience particularly when applied to debris or soil samples. The laboratory must operate to an adequate quality assurance programme and from November 2004, laboratories carrying out this test, must hold relevant accreditations from The United Kingdom Accreditation Service, UKAS.

⁽¹⁾ Health and Safety Executive (2005). HSG248. Asbestos: The analysts' guide for sampling analysis and clearance procedures. HSE Books. ISBN 0 7176 2875 2.

METHODOLOGICAL APPROACH TO THE ANALYSIS OF ASBESTOS IN ROCKS

L. Bologna¹, C. Cazzola¹, C. Clerici², E. Lauria¹, M. Wojtowicz¹

¹ ARPA Piemonte – Polo Amianto, Grugliasco (TO)

² POLITECNICO DI TORINO – Dipartimento di Ingegneria del Territorio, dell' Ambiente e delle Geotecnologie – (TO)

L'amianto, minerale di origine secondaria, quale costituente accessorio od occasionale delle rocce denominate "pietre verdi"¹, si trova, normalmente, come riempimento di macro o micro fratture di dimensioni millimetriche o submillimetriche. Sebbene quantitativamente subordinato ai minerali essenziali, come costituente è diffuso con una certa regolarità nella

¹ La dicitura "pietre verdi" indica differenti litotipi che possono contenere amianti di serpentino e di anfibolo: serpentiniti, prasiniti, eclogiti, anfiboliti, scisti actinolitici, scisti cloritici, talcosi e serpentinosi, oficalciti.

massa rocciosa. I tenori sono normalmente bassi; a Balangero, ex sito estrattivo di crisotilo, ad esempio, il tenore è del 6+8%.

L'elevata sfaldabilità degli aggregati e la loro scarsa adesione alla matrice rocciosa sono tali per cui la "perturbazione" di rocce, anche a basso tenore, può liberare notevole quantità di fibre respirabili; l'acclamata cancerogenicità delle fibre di amianto, anche per bassi livelli di esposizione, suggerisce azioni finalizzate a contrastarne la diffusione.

Di primaria importanza risulta, quindi, il problema delle attività antropiche nelle zone interessate dalla presenza di rocce contenenti amianto (amianto naturale) e la necessità di bonifica, o meglio di un ripristino ambientale, delle zone degradate (cave, affioramenti, ecc.) che possono essere sorgenti di fibre a seguito sia di fenomeni naturali sia di interventi umani.

Prescrizioni normative sulle pietre verdi sono contenute nell'allegato 4 al D.M. 14.05.96. L'indice di rilascio, funzione della percentuale di amianto rilasciato e della densità, consente di classificare i materiali in "pericolosi" e "non pericolosi". Tale norma, quindi, in deroga ai divieti posti dalla legge 257/92, ha consentito la commercializzazione di materiali in breccia, lastre e blocchi derivanti da queste rocce, classificati non pericolosi. Il D.M. n° 101 del 18.03.2003 dispone, sull'intero territorio nazionale, la realizzazione di una mappatura sia dell'amianto naturale sia di quello antropico, oltre all'individuazione dei siti che necessitano di interventi di bonifica urgenti.

L'impossibilità di sottoporre ad analisi campioni omogenei e rappresentativi, la variabilità delle caratteristiche chimiche e fisico-morfologiche dell'amianto in ambiente naturale, le interferenze strumentali dovute alla presenza contemporanea della forma fibrosa e non fibrosa dello stesso minerale, nonché la presenza di altre forme fibrose non classificabili amianto, rende difficoltoso l'intero iter analitico.

Nelle "pietre verdi" l'amianto si presenta in giaciture discontinue, le cui forme tipiche sono vene, straterelli, filoni, ecc. ponendo seri problemi di campionatura, anche quando finalizzata solo ad analisi di tipo qualitativo. Occorre evidenziare, inoltre, che i campioni primari, per quanto di volume molto piccolo, non coincidono mai con il campione analitico, ovvero con il campione di granulometria e massa adatte alle fasi analitiche.

Un minerale viene classificato come amianto quando si verificano contemporaneamente due condizioni:

- forma fibrosa;
- appartenenza ad una delle 6 specie mineralogiche indicate come amianto dalle varie normative.

Il termine amianto o asbesto indica un tipo di tessitura ovvero l'aspetto macroscopico con cui si presenta un minerale. La tessitura asbestoide si ha quando un minerale si presenta in aggregati di cristalli allungati, esilissimi, filiformi, disposti paralleli l'uno all'altro secondo l'allungamento; a volte i cristalli sono così sottili da essere addirittura pieghevoli, soffici, lanosi. La tessitura asbestoide è un caso particolare di tessitura d'aggregato presente nei minerali. Tutti i minerali fibrosi si presentano anche in forma non fibrosa, come specificato nella tabella seguente per gli amianti.

Tabella 1 – Forma fibrosa (amianti) e corrispondente forma massiva dello stesso minerale.

FORMA FIBROSA ²	FORMA NON FIBROSA
Crisotilo	Antigorite
Crocidolite	Riebeckite
Amosite	Cummingtonite – grunerite
Tremolite fibrosa	Tremolite
Actinolite fibrosa	Actinolite
Antofillite fibrosa	Antofillite

I metodi analitici utilizzabili per la determinazione dell'amianto sono indicati nel D.M. 06.09.94 e si suddividono in:

- metodi basati sulla microscopia:
 - microscopia ottica a contrasto di fase – tecnica della dispersione cromatica (MOCF-DC) e luce polarizzata (LP);
 - microscopia elettronica scansione (SEM) e trasmissione (TEM);
- metodi analitici "strumentali": diffrazione a raggi X (DRX) e spettroscopia all'infrarosso (FT-IR).

Le sopra citate interferenze strumentali dovute alla presenza contemporanea di amianto e della corrispondente forma non fibrosa, rendono la microscopia ottica particolarmente adatta alle analisi di routine; le altre metodologie forniscono un supporto indispensabile per approfondire i casi più complessi. A parere degli scriventi nessuna delle predette tecniche strumentali è proponibile, da sola, per l'analisi dell'amianto nelle rocce.

Si illustra di seguito il metodo adottato dagli autori, limitatamente all'analisi qualitativa; si basa sull'utilizzo della microscopia ottica, tecnica della dispersione cromatica, previa osservazione del materiale allo stereomicroscopio. Questa osservazione preliminare risulta fondamentale in quanto permette di agevolmente "ispezionare" il campione o aliquote rappresentative; la manipolazione diretta consente di estrarre il materiale fibroso da sottoporre ad analisi in MOCF - DC. Questa tecnica consiste nell'immersione dei fasci fibrosi in specifici liquidi ad indice di rifrazione noto. La corretta applicazione del metodo necessita di adeguata preparazione del campione, non descritta nel predetto decreto ministeriale.

Di seguito si riportano le modalità operative:

² La direttiva 2003/18/CE ha modificato come segue l'attuale nomenclatura degli amianti: crisotilo, crocidolite, grunerite d'amianto (amosite), tremolite d'amianto, actinolite d'amianto, antofillite d'amianto. Il termine per l'adeguamento degli stati membri è stato fissato al 15/04/2006.

- essiccazione del campione in stufa a 100°C. Opportuno, poiché risulta difficoltosa l'individuazione delle fibre, da sottoporre ad analisi, in un campione umido. Indispensabile in quanto la presenza di acqua d'imbibizione, altera il fenomeno della dispersione cromatica;
- individuazione con l'ausilio di una lente d'ingrandimento o meglio di uno stereomicroscopio per la contestuale separazione di un'aliquota rappresentativa, di pochi grammi, del materiale in esame. Campioni di massa contenuta possono essere sottoposti all'analisi per intero. Queste operazioni devono essere condotte sotto la cappa aspirante;
- osservazione, allo stereomicroscopio, dei campioni (o delle aliquote), inizialmente a bassi ingrandimenti (6÷10X) ed eventualmente ad ingrandimenti maggiori. Separazione mediante bisturi e pinzette del materiale fibroso;
- sistemazione del materiale sul vetrino. I fasci fibrosi devono essere aperti ed appiattiti; questo favorisce la messa a fuoco del preparato al microscopio e risulta fondamentale per poter osservare i colori derivanti dal fenomeno della dispersione cromatica;
- dispersione delle fibre nel liquido ad indice di rifrazione noto. La scelta del/i liquido/i opportuno/i è effettuata in dipendenza dell'aspetto morfologico del materiale fibroso in esame;
- osservazione del preparato al microscopio ottico, in dispersione cromatica. L'osservazione è normalmente condotta a bassi ingrandimenti (100 X); solo occasionalmente, per osservare fibre atipiche, degradate o contaminate, è utile passare ad ingrandimenti maggiori. La caratteristica colorazione delle fibre e degli aloni, che varia in modo tipico in relazione alla posizione della fibra rispetto al piano di vibrazione della luce polarizzata e la contemporanea valutazione della morfologia delle fibre, permettono di stabilire, se le fibre osservate sono di amianto e a quale tipologia appartengono.

Generalmente la procedura indicata risulta sufficiente ad individuare l'amianto e definirne la tipologia. Tuttavia, trattandosi di campioni naturali, non è raro riscontrare strutture fibrose con caratteristiche fisiche solo parzialmente riferibili all'amianto; si deve in questi casi procedere ad approfondimenti analitici facendo uso delle altre tecniche.

Con le tecniche strumentali (FT-IR e DRX), considerato che la roccia madre fornisce risposta analitica molto simile a quella dell'amianto, è buona norma, onde evitare errate interpretazioni, lavorare sul materiale fibroso isolato, durante l'osservazione allo stereomicroscopio.

Nel caso di ricorso alla microscopia elettronica a scansione non solo è consigliabile utilizzare esclusivamente il predetto materiale isolato, ma è oltremodo opportuno procedere ad un'accurata deposizione sullo stub, al fine di favorire l'osservazione delle strutture fibrose ad elevati ingrandimenti e di effettuare la microanalisi, che consente la caratterizzazione chimica, su "singoli" individui.

In conclusione, nei casi più complessi, per avere una caratterizzazione soddisfacente, è necessario acquisire le informazioni fornite dalle diverse metodiche analitiche.

QUANTITATIVE DETERMINATION OF ASBESTOS IN ROCKS AND SOILS BY OPTICAL MICROSCOPY: ANALYTICAL METHODS AND EXAMPLES OF APPLICATION

C. Cazzola¹, C. Clerici¹, S. Francese¹, M. Patrucco¹, G. Zanetti¹, F. Gallarà²

¹ Politecnico di Torino – Dipartimento di Ingegneria del Territorio, dell'Ambiente e delle Geotecnologie

² LTF s.a.s – TORINO

Another paper presented at this congress explains the operational principles and the analytical methods for the quantitative determination of the asbestos content in rocks. This paper represents a further contribution to this topic, as it illustrates a method based on optical microscopy with which semiquantitative results can be obtained.

The quantitative analysis of the asbestos content in rocks and soils is more and more required, even when this content is extremely low. For instance according to an Italian law concerning polluted soils (L. 471/99) it must be established if the asbestos content (free fibres) is higher or lower than 0,1%. In these cases optical microscopy can be useful, even if it has been criticized for being a subjective and impossible to standardize method.

On the other hand, optical microscopy has the following benefits:

- it is not influenced by interference between fibrous and non fibrous asbestos minerals;
- it is possible to distinguish between free fibres and fibres included in a matrix;
- even very low asbestos contents can be detected with a sensitivity which is not attained by other analytical methods.

The difficulties encountered in transforming into content by mass the results obtained by counting the particles, which are inherent in all microscopic methods (including electron microscopy) can be – at least partly – overcome using the analytical method here described.

The following operational principles are assumed as a basis.

- 1) For a microscopical analysis one must see the particle. Therefore if the asbestos fibres are included in a matrix the sample must be ground to a size at which the liberation of the asbestos fibres from the matrix is attained. That means that the comminution product must be formed either by asbestos particles or matrix particles, without middlings. If the aim of the analysis is to determine "free" fibres, no grinding is performed, otherwise the degree of liberation of the components and therefore also of the asbestos will increase.
- 2) The comminution product is then classified into close size ranges by means of wet screening. This will make easier the analysis, as each class is formed by particles having similar sizes. Wet sieving is used for the following aims:

- to obtain a well classified product;
- to prevent dispersion of fibres in the air.

The number of classes and the limiting sizes of the classes are chosen taking into account the nature of the material and the aim of the analysis.

Each class is examined under the optical microscope, using different methods as a function of the size:

- for the coarse classes the fibres are sorted using a stereomicroscope and the sorted product is examined using phase contrast microscopy with chromatic dispersion (PCOM) in order to verify if all the sorted fibres are asbestos fibres; the asbestos content by mass of each class can be obtained by weighing the sorted products;
- for the intermediate classes the fibres are counted using an optical microscope both in polarized light and in phase contrast (the number of asbestos tufts is given as a percentage of the total number of particles). To obtain the asbestos content by mass the volume of the asbestos tufts can be evaluated by comparison with nearby non-asbestos particles. By the use of polarized light optical microscopy (PLOM) it's also possible to determine the particle thickness by inserting the analyzer and observing the birefringence phenomenon, which gives a rough estimate of the particle thickness. In conclusion it is possible to say that an asbestos tuft has the same mass as two non fibrous particles or a particle, or half a particle;
- for the finest class (e.g. < 400 mesh) the procedure is more difficult because there is no lower limit to the particle size. Also in this case the asbestos fibres are identified in PCOM and counted. The volume of each fibre is determined by using an eyepiece micrometer. To obtain the asbestos content by mass the microscope specimens are previously weighted on an analytical balance.

An example the analytical results obtained on a sample of a slurry produced by washing aggregates in a crushing plant of serpentine rocks are given in table 1.

The sample has been sieved with 28,48,100,200 and 400 mesh sieves; due to the high content of fine particles also a sieving with a 20 micrometers mesh sieve has been performed.

Figures from 1 to 5 show examples of microscopic fields: figures from 1 to 4 are in PLOM (analyzer inserted) while figure 5 is in PCOM.

The average asbestos content in the sample is given by the weighted mean of the contents in the size classes. The table also shows the asbestos distribution in the different classes. It is therefore possible to find out in which classes most of the asbestos minerals are present. Deeper analysis, if needed, will be carried out only on these classes.

Table 1- Analytical results on a slurry sample.

size classes	mass (%)	asbestos content (mg/kg)	asbestos distribution (%)	type of asbestos
> 28 mesh	17.54	0	0	-
28 – 48	1.55	0	0	-
48 – 100	1.82	100	0,4	chrysotile
100 – 200	2.22	353	1,9	chrysotile
200 – 400	6.81	1775	29,5	chrysotile
400 – 20 µm	26.02	508	32,2	chrysotile , tremolite
<20 µm	44.04	334	36,0	chrysotile

The figures show how it is easy to detect at a glance fibrous tufts or isolated fibres in PLOM by inserting the analyser; if the same field is afterwards observed in PCOM the nature of the fibres can be determined through the chromatic dispersion phenomenon. Also the shape can be easily detected and this is useful for the evaluation of the particles mass.

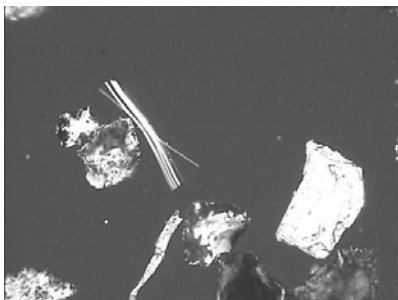


Photo 1. 48 - 100 mesh class. A frayed chrysotile tuft (at the centre) and an organic fibre (below). Short side of the photogram 0,94 mm.

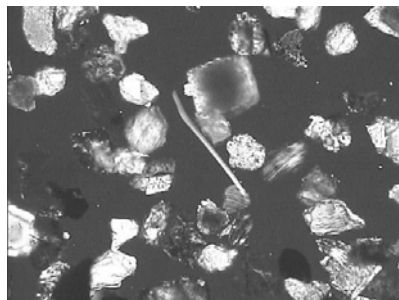


Photo 2. 100 - 200 mesh class. A thin chrysotile tuft at the centre. Short side of the photogram 0,94 mm.

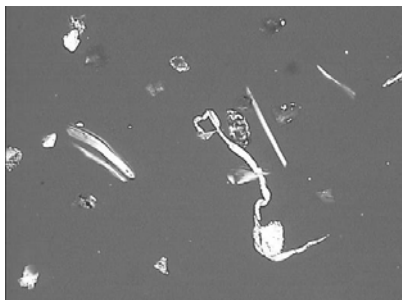


Photo 3. 200 – 400 mesh class. Chrysotile tufts and an organic fibre (at the centre and below). Short side of the photogram 0,94 mm.

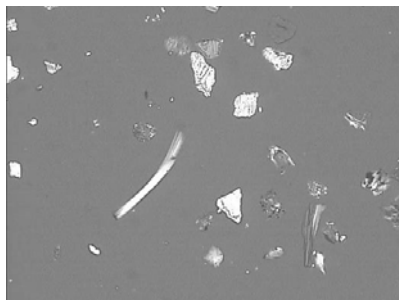


Photo 4. 400 mesh – 20 micrometers class. A partly frayed chrysotile tuft. Short side of the photogram 0,47 mm.

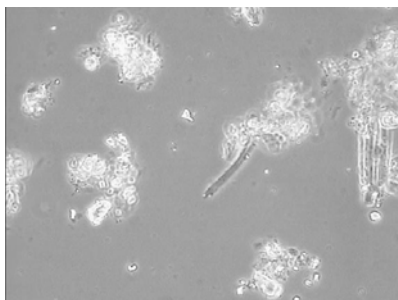


Photo 5. < 20 micrometers class. At the centre a chrysotile tuft (blue with an orange halo). Short side of the photogram 0,235 mm.

QUANTITATIVE ANALYSIS OF FIBROUS MINERALS IN ROCK SAMPLES USING BSE IMAGES AND μ -RAMAN SPECTROSCOPY

Chiara Groppo^{1,3}, Roberto Compagnoni^{1,3}, Bice Fubini^{2,3}, Maura Tomatis^{2,3}, Laura Bruna⁴, Paolo Piazzano⁴, Giorgio Schellino⁴

¹ Dept. of Mineralogical and Petrological Sciences, University of Torino, Torino, Italy

² Dept. of Chemistry IFM – University of Torino, Torino, Italy

³ Interdepartmental Center "G. Scansetti" for Studies on Asbestos and other Toxic Particulates - University of Torino, Italy

⁴ Regione Piemonte, Torino, Italy

The quantitative determination of asbestos in rocks is of paramount importance in evaluating of the asbestos hazard in the natural environment. The traditional techniques commonly used - FTIR spectroscopy and X-Ray powder diffraction - do not preserve the microstructural information, which is essential in case of minerals occurring with both fibrous and prismatic habit, such as antigorite and tremolite.

To quantify the fibrous minerals in serpentinites from the western Alps, two different techniques have been combined:

- 1) electron back-scattered (BSE) images, acquired at SEM, which give morphological and compositional data for each particle of the powdered samples;
- 2) μ -Raman spectroscopy, which is able to identify unambiguously the fibrous minerals, especially those of the serpentine group.

This method was tested on a serpentinized peridotite from the low Susa Valley (Western Alps) crosscut by a network of chrysotile asbestos veins. The rock sample was grinded in a mill for three hours; the obtained powder was mixed with boric acid (H_3BO_3) and transformed into a pellet. The boric acid has been chosen as a matrix because i) it gives a very weak signal if observed at SEM in back-scattered electron (BSE) mode, and ii) its Raman peaks lie in frequency regions (501 and 880 cm^{-1}) non interfering with the serpentine bands.

The pellet was observed at SEM and BSE images were acquired. BSE images show that the sample mainly consists of serpentine minerals, with both lamellar and fibrous habit. The chemical difference between lizardite and chrysotile is too low to produce a image contrast useful in the serpentine type identification. Micro-Raman spectra have also been acquired on several particles in the frequency interval $300 - 800\text{ cm}^{-1}$, using a 632.8 nm laser, and 7 scans for 10 seconds. In spite of the very rapid acquisition time, for each particle the acquired Raman spectra are sufficient to identify

the serpentine minerals. The SiO_4 tetrahedra bending modes of lizardite and chrysotile, in fact, occur at 388 cm^{-1} and 393 cm^{-1} , respectively.

Image analysis of two BSE images was performed using the software Scion Image (Scion Corporation, Frederick, Maryland). For each particle previously analysed by micro-Raman technique area, maximum and minimum axis have been determined. The percentage of chrysotile was calculated from the area of the particles identified as chrysotile on the basis of the Raman spectra divided by the total area of the particles.

This method, only preliminary tested, may be very useful if applied to antigorite serpentinites, in which both antigorite and chrysotile occur with fibrous habit.

RAMAN SPECTROSCOPY: A RAPID TECHNIQUE TO IDENTIFY ASBESTOS PHASES

Caterina Rinaudo^{1,3}, Daniela Gastaldi¹, Simona Cairo¹, Chiara Groppo^{2,3}, Roberto Compagnoni^{2,3}, Elena Belluso^{2,3}

¹ Department of Life and Environmental Sciences – Università del Piemonte Orientale “Amedeo Avogadro” – Via Bellini 25/G - 15100 Alessandria - Italy

² Department of Mineralogical and Petrological Sciences - Università di Torino - Via Valperga Caluso 35- 10125 Torino - Italy

³ Interdepartmental Center “G. Scansetti” for Studies on Asbestos and other Toxic Particulates – Università di Torino - Italy

The Raman effect was discovered in 1928 by the Indian physicist C. V. Raman, who noticed that after a beam of light is absorbed and released by a substance, a tiny portion of the scattered light differs in wavelength from the incident beam [1]. This shift in wavelength, known as *Raman scattering*, is independent from the excitation source wavelength and is determined by vibrations of the chemical bonds constituting the crystalline structure. The Raman spectrum is thus characteristic for each substance and serves as a unique fingerprint for the characterization of materials in physical and chemical research. Raman spectroscopy has several advantages: it can be applied to the study of liquid, solid and gaseous phases, is quick and requires no special sample preparation. In fact, to obtain a Raman spectrum one need only place the specimen in the path of the incident laser beam in a spectroscope. What's more, coupling of an optical microscope with the spectroscopy allows the Raman spectrum to be recorded on an optically-selected portion of the sample, making it easy to identify heterogeneities in the samples analyzed.

In this work, Raman spectroscopy has been applied to the study of asbestos minerals, whose identification by conventional techniques (i.e., XRPD, SEM-EDS and TEM-EDS) is time-consuming, requires careful sample preparation and poses the risk for artefacts. The technique proves especially useful in the analysis of asbestos minerals - actinolite, amosite, anthophyllite, crocidolite, tremolite and chrysotile - because no need for contact with the sample is required, thus minimizing the risk for inhalation of potentially toxic small fibres. The study relies on samples previously characterized by XRPD, SEM-EDS, TEM-EDS, in order to guarantee the identity of the mineral phase on which the Raman spectrum was registered. Three separate experiments [2-4] prove that the Raman spectroscopy is reliable in identifying the different phases of asbestos, despite extreme similarity in the mineral's chemical and crystallographic composition. In fact by analysing the frequencies of the bands produced by vibrations of the symmetric stretching modes (ν_s) – frequencies ranging from 600 cm^{-1} to 700 cm^{-1} - and of the anti-symmetric stretching modes (ν_{as}) – frequencies ranging from 1000 cm^{-1} to 1150 cm^{-1} - of the different Si-O-Si linkages [5, 6] that make up the crystalline structure, the asbestos phase can be unequivocally identified. The characteristic spectra obtained from the pure mineral phases in these experiments (Fig. 1) are then used as reference spectra for further applications, including the identification of asbestos minerals in rocks, building materials and organic tissues.

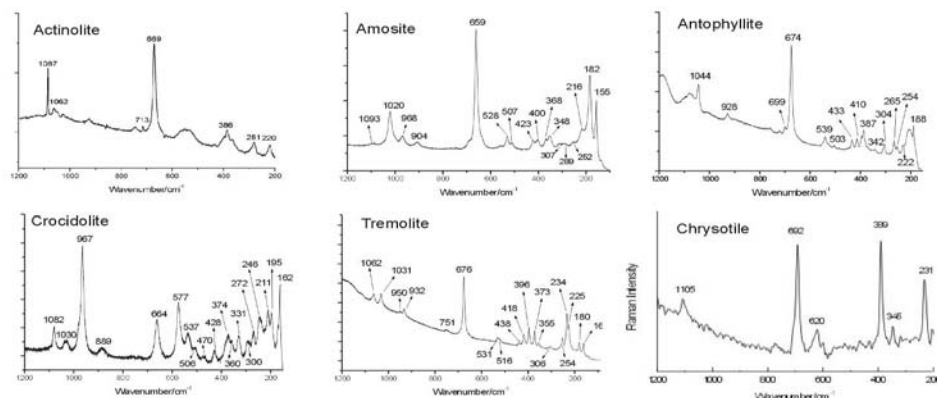


Figure 1 – Raman spectra obtained from pure asbestos phases.

- 1) Serpentine minerals in rock samples are often difficult to be identified because of their similar optical properties, the presence of sub-microscopic intergrowths and their fine grain. Micro-Raman spectroscopy has been applied on thin sections of minerals, allowing a reliable and rapid identification of lizardite, antigorite and chrysotile, even when they are microscopically intergrown or form aggregates with other minerals. It should be noted that this technique allows preservation of the microstructural informations. It is therefore also preferable to analytical techniques such as XRPD and IR, which require sample grinding, as well as to the more time-consuming TEM-EDS technique. Micro-Raman spectroscopy thus proves to be the best technique to date for study of the ultramafic system, which cannot be unambiguously characterized by optical microscopy and/or SEM-EDS [7].
- 2) Different building materials containing fibres underwent μ -Raman characterization. An example on a fragment of cement used as roofing material and containing fibres is shown [8]. In this case, too, the results obtained with Raman spectroscopy were compared with those obtained by using the more conventional XRPD, SEM-EDS and TEM-EDS techniques. As can be seen in Fig. 2, when the laser beam was directed on the thick part of the optically observed fibres a Raman spectrum attributable to crocidolite fibres was registered – spectrum A in Fig. 2. When the laser beam was directed on the thinner part of the fibre, bands attributable to crocidolite fibres and cement matrix - CaCO_3 and circled on spectrum B, Fig. 2 - appear on the same spectrum. Moreover the spectrum registered on the finest fibres, as observed optically, also showed bands attributable to the chrysotile phase- spectrum C in Fig. 2. The XRPD, SEM-EDS, and TEM-EDS techniques confirmed the results of Raman spectroscopy: the phases constituting the analyzed sample were crocidolite, chrysotile and calcium carbonate.

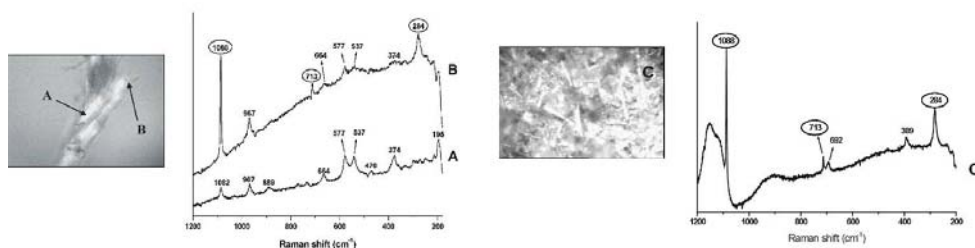


Fig. 2- Raman spectra obtained on the material fragment studied: spectrum A corresponds to crocidolite; spectrum B is attributable both to crocidolite and to CaCO_3 (circled bands); C corresponds to chrysotile and CaCO_3 .

- 3) Studies of the application of Raman Spectroscopy for the identification of fibres in pulmonary tissue from patients affected by mesothelioma or other pulmonary diseases are in progress, but the preliminary findings are very promising.

Taken together, the present results indicate that Raman spectroscopy is an extremely useful technique for the quick and reliable identification of asbestos phases in different matrices.

References:

- [1] Colthup, N.B., Daly, L.H., Wiberley, J.E. (1990) Introduction to Infrared and Raman Spectroscopy, Academic Press, New York.
- [2] Rinaudo, C., Gastaldi, D. & Belluso, E. (2003) Characterization of chrysotile, antigorite and lizardite by FT-Raman Spectroscopy, Canadian Mineralogist, 41, 883-890.
- [3] Rinaudo, C., Gastaldi, D. & Belluso, E. (2003) La spettroscopia Raman: tecnica di identificazione rapida di fibre di asbesto, Siti contaminati, 2, 116-120.
- [4] Rinaudo, C., Belluso, E. & Gastaldi, D. (2004) Assessment of Raman spectroscopy on asbestos of known chemistry and mineralogy, Mineralogical Magazine, 68 (3), 455-465.
- [5] Farmer, V. C. (1974) The infrared spectra of minerals, Mineralogical Society Ed., London.
- [6] Lazarev, A. N., (1972) Vibrational spectra and structure of silicates, Consultants Bureau, New York and London.
- [7] Groppo, C., Rinaudo, C., Cairo, S., Gastaldi, D. & Compagnoni, R. Micro-Raman Spectroscopy as a new rapid method for the identification of serpentine minerals from serpentinized ultramafics, submitted to European Journal of Mineralogy
- [8] Rinaudo, C., Gastaldi, D., Belluso, E. & Capella S. (2005) Application of Raman Spectroscopy on asbestos fibre identification, Neues Jahrbuch fur Mineralogie, 182/1, p. 31-36.

Session: Analysis in liquids

S. Malinconico	International and Italian regulations concerning asbestos limits in liquids
A. Brancia	Determination of asbestos in water by FT-IR technique: a proposal for an analytical routine-model
O. Sala	Investigations on the occurrence of asbestos fibers in drinking water
L. Zamengo	Analysis of asbestos fibres in hazardous waste landfill leachates: the FALL project

INTERNATIONAL AND ITALIAN REGULATIONS CONCERNING ASBESTOS LIMITS IN LIQUIDS

S. Malinconico¹, F. Cappa¹, L. Zamengo²

¹ ISPESEL - Istituto Superiore per la Prevenzione e la Sicurezza sul Lavoro - Roma, Italy

² Physical Chemistry Department, Università Ca' Foscari, Venezia, Italy

FALL (Filtering of Asbestos fibres in Leachate from hazardous waste Landfills) is a project financed with European funds within the LIFE Program, a Financial Instrument for the Environment that contributes to the implementation, development and enhancement of the Community environmental policy and legislation, as well as the integration of the environment into other EU policies. One of the main objectives of the FALL project is the definition of analytical procedures for asbestos quantitative determination in leachates, which can be helpful to the definition of a community protocol aiming at regulating this matter.

During the first stage of the project the most significant studies concerned with the presence of asbestos fibres in liquids and their potential dangerousness were examined. We need to underline that, while the carcinogenicity induced to the respiratory system by inhaled asbestos fibres has been experimentally demonstrated, the danger for the gastrointestinal tract due to ingestion of such fibres is still under discussion. According to the World Health Organization (WHO), epidemiological studies do not support the hypothesis of an increased cancer risk associated with the ingestion of asbestos in drinking-water. Moreover, in extensive feeding studies in animals, asbestos has not consistently increased the incidence of tumours of the gastrointestinal tract. Since there was no clear evidence that ingested asbestos is hazardous to health, no guideline for asbestos in drinking-water was established by the WHO [1].

However, some studies on the subject, some of which very recent, have established a correlation between the increase in the onset of gastrointestinal cancers and the ingestion of fibres, mainly contained in drinking water [2] [3] [4]. For this reason, asbestos was inserted in the list published in a recent Italian decree (27/04/2004; GU n. 134, 10/6/2004) describing professional illnesses for which reporting to the controlling Authority is mandatory, as causal agent of cancers of gastroenteric nature with a possible origin in working activities. The list includes occupational cancers for which the epidemiological investigations proved a link to working activities, even if only presumed.

Furthermore, some attention has been currently drawn to the possibility of aerodispersion during transfer or treatments of asbestos-containing liquids, for instance by formation of aerosol.

International regulations have not fixed limits particularly restrictive to the content of asbestos fibres in liquids.

In the U.S.A., asbestos in water is classified as a Category II contaminant, based on evidence from the National Toxicology Program (NTP) dietary and drinking water ingestion studies. Considering a risk level of 10^{-6} , based on a daily consumption of two litres of drinking water in lifetime, the U.S. EPA in the corresponding interim Ambient Water Quality Criteria (AWQC for ingesting water and organisms) established in 1980 a limit of 30.000 fibres/litre [5]. In 1991 the U.S. Environmental Protection Agency (EPA) promulgated drinking water standards which included a Maximum Contaminant Level (MCL) for asbestos of 7 Millions of Fibres per Litre (MFL) based only on fibres longer than 10 μm . However, more than 95% of waterborne asbestos are usually shorter than 10 μm , and the U.S. EPA 100.1 TEM analysis method considers fibres longer than 0.5 μm .

The Ambient Water Quality Criteria for Asbestos (U.S. EPA, 1980) [6] stated an average correspondence of 0,12 mg asbestos/ m^3 to 2 fibres/ml, picking up the standard proposed by the British Occupational Hygiene Society (BOHS).

The Council of the European Union issued in 1987 a Directive on the prevention and reduction of environmental pollution by asbestos (87/217/EEC). The Directive controls emissions of asbestos to air and water. Regarding aqueous effluents, the limit value is 30 g total suspended matter per m^3 of effluent, with a conversion factor of two fibres/ml to 0,1 mg/ m^3 of asbestos dust, corresponding to $600 \cdot 10^6$ fibres/litre. For the purposes of the Directive a fibre is defined as any object of length larger than 5 μm , width smaller than 3 μm , and having a length/width ratio larger than 3:1, which is countable by phase contrast optical microscopy by using the European reference method defined in Annex I of the 83/477/EEC Directive. Competent authorities must specify the maximum volume of discharge into water of the total quantity of suspended matter per tonne of products.

The 87/217/EEC Directive was implemented in Italy by a decree (DL 17/3/1995, n. 114), which fixes the limit values in wastewater from industrial and remediation activities. Nevertheless, competent authorities may set different limits by referring to the Italian law n. 257/1992, art. 3 §3, appealing to the particular nature of the asbestos-containing products present in the wastewater.

Documents for the adoption of a more restrictive limit have been recently submitted to the Environmental Ministry (Ministero dell'Ambiente e Tutela del Territorio, MATT) during official meetings concerning the national interest sites "Bari Fibronit" and "Biancavilla Etnea". Regarding Bari Fibronit, reference was made to the indications of the Regional Agency for Environmental Protection (ARPA Toscana) reporting a study by the Safe Drinking Water Committee of the U.S.A National Academy of Sciences, according to which a limit of 200.000 fibres/litre can induce gastrointestinal tumor in a ratio 1/100.000 on inhabitants whose drinkable water consumption is 2 litre/day on a 70 years span. During the official meetings concerning the Biancavilla Etnea site, observations by ARPA Piemonte based on [7] have been accepted, according to which values of 100.000 fibre/litre in the liquids determine a release of around 2 fibre/litre in air, which is the current legal limit for the restitution of buildings after remediation (Decreto Ministero Sanità 6/9/1994).

No threshold has been identified for carcinogenic risks with regard to asbestos. This means that no exposure to asbestos, no matter how small, can be assumed to be safe. Considering this and all the above referred, the adoption of lower limits for the presence of asbestos in water, should be a requirement for future environmental and health guidelines, laws and regulations.

- [1] WHO, Asbestos in Drinking-water; Background document for development of Guidelines for Drinking-water Quality (2002)
- [2] J.S. Webber, Asbestos contaminated drinking water, Handbook of hazardous materials (1993)
- [3] K. Kjaerheim et al., Cancer of the gastrointestinal tract and exposure to asbestos in drinking water among lighthouse keepers (Norway). Cancer Causes Control, 16(5):593-598). (2005)
- [4] K. P. Cantor, Drinking water and cancer - Cancer Causes and Control, 8, pp. 292-308 (1997)
- [5] quoted in: California Environmental Protection Agency, Draft For Review Only - Public Health Goal for ASBESTOS In Drinking Water Prepared by Pesticide and Environmental Toxicology Section Office of Environmental Health Hazard Assessment (June 2002)
- [6] U.S. EPA - Ambient Water Quality Criteria for Asbestos (1980)
- [7] J.S. Webber, S. Syrotynski, M.V. King, Asbestos contaminated drinking water: Its impact on household air, Environ. Res. 46:153-167. (1988)

Contacts:

Dott. S. Malinconico: ser.malin@libero.it

Dott. ing. F. Cappa: fkappa@libero.it

Dott. L. Zamengo: zamengo@unive.it

EU Project web-site : www.unive.it/fall

DETERMINATION OF ASBESTOS IN WATER BY FT-IR TECHNIQUE: A PROPOSAL FOR AN ANALYTICAL ROUTINE MODEL

A. Brancia

B.e.t.a s.r.l., Napoli, Italy

L'utilizzo ormai ultradecennale di condotte in materiali contenenti amianto per la distribuzione di acque potabili oltre che per il convogliamento dei reflui urbani pone la questione della determinazione non solo della presenza ma soprattutto del tenore in amianto dell'acqua stessa. Inoltre, è sempre più frequente la necessità di determinare il contenuto di amianto nelle acque reflue provenienti dai sistemi di filtrazione degli impianti di lavaggio nei cantieri di bonifica, che resta fissata dalla vigente normativa solo come solidi sospesi totali, a ns. avviso non sufficientemente cautelativi, nonché delle acque di dilavamento dei siti di conferimento di MCA.

L'adozione di tecniche e strumentazioni di comune impiego nei laboratori può essere opportunamente impiegata anche per definire una metodica che consenta agevoli analisi di routine con limiti di rivelazione sufficientemente sensibili.

Il presente lavoro descrive l'iter procedurale attuato presso il ns. laboratorio, anche mediante la preparazione di soluzioni acquose a titolo noto di materiali asbestosici, le modalità di preparazione dei campioni opportunamente modulate in funzione della origine merceologica primaria delle acque trattate, le tecniche adottate per la quantificazione in % peso dell'amianto e i risultati ottenuti.

Per la filtrazione delle acque sono state impiegate normali beute per filtrazione, collegate a pompa da vuoto ad acqua, con supporto portamembrana in acciaio inox e bicchiere tarato da filtrazione. Il supporto filtrante adottato è costituito da membrane in nitrato di cellulosa con porosità di $0,45 \mu$. Le pesate sono state eseguite mediante bilancia con sensibilità di 1×10^{-5} g.

Sono state allestite soluzioni acquose a titolo noto di materiali asbestosici, ricavati dai campioni di materiale esistenti presso il nostro laboratorio, per i quali è stato determinato il contenuto e il tipo di amianto mediante spettrofotometria all'infrarosso con trasformata di Fourier (FTIR); sono stati scartati quelli aventi tenore complessivo inferiore al 95% in peso e/o struttura semicompatta (teli, cordoni, trecce). I materiali prescelti sono stati sottoposti a blando trattamento in mortaio di agata dopo essiccazione in stufa a 105°C per 12 ore, per facilitarne la disperdibilità nel liquido.

Per l'allestimento delle soluzioni, sono state utilizzate sia normali acque da rete idrica, anche addizionate con prodotti detergenti di uso comune, sia acque provenienti da vasche di raccolta reflui sicuramente esenti da Materiali Contenenti Amianto. La verifica dell'assenza di fibre asbestosiche nelle matrici acquose di prova è stata eseguita mediante esame in Microscopia Ottica in Contrasto di Fase di membrana attraverso la quale è stato filtrato il liquido.

Successivamente, sono state predisposte soluzioni a diluizioni successive dei liquidi a titolo noto così preparati, sia con acque da rete idrica che con reflui, privati degli eventuali materiali grossolani mediante prefiltrazione con setaccio a maglie di mm. 2. Per l'allestimento e la conservazione delle soluzioni di lavoro sono stati utilizzate taniche da lt.5.

Le soluzioni di lavoro così ottenute sono state sottoposte a filtrazione, in numero di 6 per ciascuna soluzione, ed i filtri, a coppie, sono stati messi in stufa non ventilata a 60°C per 2, 12 e 24 h.

Dopo il trattamento in stufa, sono stati aggiunti mg. 200 di KBr a ciascuna membrana e si è provveduto a trattare in mortaio d'agata il tutto fino alla dissoluzione visiva della membrana (circa 20 minuti), ottenendo quindi pasticche mediante fusione per 15 minuti a 10 ton che sono state sottoposte ad analisi in FTIR.

Come "bianco" è stato adottato filtro a membrana dello stesso lotto, vergine, sottoposto a filtrazione di pari volume di acqua distillata.

I risultati analitici, visualizzati in assorbanza, sono stati selezionati nel range di numeri d'onda compresi tra 3550 e 3900 cm^{-1} , atteso che la matrice ha evidenziato notevole assorbanza per i numeri d'onda più alti.

In particolare, la presenza di picco tra 3683 e 3691 cm^{-1} è stata considerata caratteristica del crisotilo, la presenza di picco a 3676 cm^{-1} caratteristica dell'antofillite, la presenza di picchi a 3618 cm^{-1} , 3637 cm^{-1} e 3651 cm^{-1} dell'amosite,

a 3618 cm^{-1} , 3633 cm^{-1} e 3651 cm^{-1} della crocidolite, a 3672 cm^{-1} della tremolite. Le curve di calibrazione sono state pertanto rielaborate secondo le aree sottese dai minimi di tali picchi.

Nella tabella che segue riportiamo l'esito della sperimentazione in funzione dei tempi di essiccazione rispetto al risultato atteso:

titolo presunto	2h	12h	24h
2 mg/L	$1,62 \pm 0,14$	$1,88 \pm 0,10$	$1,81 \pm 0,15$
5 mg/L	$4,33 \pm 0,75$	$4,55 \pm 0,38$	$4,64 \pm 0,22$
10 mg/L	$10,09 \pm 0,18$	$9,86 \pm 0,42$	$9,70 \pm 0,35$
50 mg/L	$51,80 \pm 2,24$	$50,49 \pm 1,39$	$50,12 \pm 0,77$
100 mg/L	$103,41 \pm 2,60$	$101,92 \pm 2,06$	$100,84 \pm 1,11$

Come si può notare, per le minori concentrazioni si è avuta generalmente un risultato inferiore a quello atteso, mentre l'opposto è accaduto per le concentrazioni maggiori. Facendo le debite riserve sulla precisione di dispersione dei materiali aggiunti alle matrici, variabili, non quantificabili, si osserva che nelle maggiori concentrazioni un minore tempo di essiccazione sembra indurre una sovrastima del dato teorico, e questo potrebbe essere motivato dall'estrema idrofilia degli asbesti, che sembrano trattenere quantità di acqua sensibili: infatti, la deviazione risulta decisamente più contenuta nell'esame dopo 24 ore di essiccazione.

Si è altresì notato che la miscelazioni in reflui anziché in acque di lavaggio simulate sembra incidere sulla sovrastima, ma questo dato è verosimilmente imputabile alla presenza, nei reflui stessi, di altri silicati misti (probabile presenza di polveri di tufo giallo napoletano).

Dal punto di vista applicativo, appare piuttosto evidente che sia nel caso di reflui potenzialmente contaminati in quantità notevoli (percolamento da discariche etc.) sia nel caso di reflui solo blandamente contaminabili (acque di scarico da cantieri di bonifica) è opportuno procedere ad essiccazione per almeno 24 h.

Il vantaggio di questa metodica rispetto alla tradizionale conta delle fibre eseguita da altri Autori è la praticabilità operativa, in particolar modo rispetto alla microscopia ottica in contrasto di fase, che nel caso di acque reflue può risultare molto disagiata, se non decisamente faticosa, per l'operatore. Inoltre, se –come ci auguriamo– sarà fissato un valore limite per le acque potabili, esso sarà ragionevolmente espresso in n° di fibre su unità di volume, mentre per le acque reflue, in analogia con quanto attualmente vigente in Italia, potrebbe risultare sufficiente un limite espresso come peso sull'unità di volume, anche al fine di ridurre i costi di analisi con tecniche microscopiche.

INVESTIGATIONS ON THE OCCURRENCE OF ASBESTOS FIBERS IN DRINKING WATER

O. Sala⁽¹⁾, E. Guberti⁽²⁾, G. Pecchini⁽¹⁾, T. Bacci⁽¹⁾, V. Biancolini⁽¹⁾, F. Paoli⁽¹⁾, E. Renna⁽¹⁾, D. Ferri⁽³⁾, Mara Veronesi⁽²⁾, A. Marconi⁽⁴⁾

¹ ARPA Sezione prov. Reggio Emilia

² ARPA Sezione prov. Bologna

³ Azienda USL Bologna

⁴ Istituto Superiore di Sanità - Roma

Researches on the occurrence of asbestos in drinking waters are widely carried out in Italy and in many other Countries. The obtained results evidence "natural pollution" phenomena due to local geological setting and pollution phenomena due to the utilization of concrete/asbestos in water pipelines.

EPA in USA in 1989 proposed a maximum contamination level limit (7 million of fibers / liter characterized by length > 10 microm.) (Collins et al, 2000); the analytical method for the determination of asbestos fibers in waters was set up in 1994 (EPA, 1994) and is based on fibers counting by ETM (Electronic Transmission Microscopy) after preliminary preparation.

Available data in Italy are scarce and chiefly related to specific studies carried out by Scanning Electronic Microscopy (SEM). (Paoletti et al, 1996; Cherubini et al, 1998; Buzio et al, 2000).

Italian law on drinking waters doesn't consider asbestos as a parameter for evaluating potability.

Law DM 14/5/96, enclosure 3, refers to OMS which states that "... there is no serious evidence that asbestos ingestion is dangerous for health, thus it was not considered useful to establish a guide value based on health considerations for the occurrence of this substance in drinking water".

Italian law furthermore consider possible fibers release from tubes or tanks in concrete/asbestos chiefly related to water aggressiveness. This parameter was already considered in previous Ministerial Circular n.42 in 1986.

Law DM 14/5/96 compels local authorities to check the status of preservation of water pipelines and to quickly change tubes and tanks in concrete/asbestos.

To this purpose the Bologna Health and Safety Service (USL Agency), considering that local water pipelines, which reach 400.000 inhabitants, are characterized by one third of tubes made by concrete/asbestos, started in 1998 the periodic sampling and analysis in 24 sampling points and in three wells. The periodic control is still ongoing. Three points have been periodically and systematically sampled by 1998 to 2005, other points have been less frequently considered for limited time periods.

The analysis of asbestos fibers counting by SEM were carried out by ARPA laboratories in Reggio Emilia while ARPA laboratories in Bologna analyzed water aggressiveness index.

The data on seven year of research of asbestos fibers related to water aggressivity in 188 samples collected in the period 1998- June, 2005 are an interesting data set useful for some considerations.

Eleven samples, the 5.8%, were positive (Fig.1 and Fig.2).

Positive samples were collected in 5 sampling points where a single positive value was obtained, further controls were negative. In another sampling point (sixth) repeated positive values were obtained in the period 1998-2004.

In the remaining 94% ca of analyzed samples were not found asbestos fibers, probably due to fact that local pipeline water is hard, scaling and poorly aggressive, thus naturally contrasting fibers release processes in concrete/asbestos.

The six repeated positive values out 24 samplings in a particular sampling point were due to peculiarities of the sampling point. It was a terminal tube located in the historical center and able to increase asbestos fibers accumulation due to recurrent fractures in tubes.

Local municipal water Agency repeatedly cleaned the tubes and apparently solved the malfunctioning. Successive controls were positive thus the problem was managed by more appropriate pipeline treatment. In order to reduce cracks frequency and water losses water pressure was reduced in the historical center of the town. In order to improve water flow in tubes better links to tube network were set up. Last five sampling (June 2004-June 2005) were negative for asbestos fibers. The maximum observed value in the 11 (5.8%) positive samples was 2550 fibers/liter, largely lower than the only suggested limit of 7.000.000 fibers/liter, above all because the fibres counted are "any fibres", not only length > 10µm.



Figure 1. Chrysotile asbestos fiber by SEM

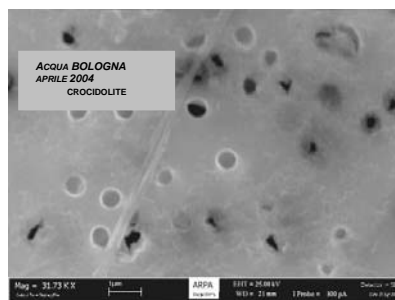


Figure 2. Crocidolite asbestos fiber by SEM

In the absence of reference methods in Italy and Europe, ARPA laboratory of Reggio Emilia has utilized a proper method for asbestos fiber counting which is different to EPA method which should be better and more appropriately evaluated.

In spite of limitations due to internal analytical method controls on Bologna waters pipeline are still on going and the asbestos monitoring activity is retained useful for preventing pollution phenomena and public health problems.

Several towns, among them Bologna and Forlì, are characterized by the presence of water pipelines made by concrete/asbestos and the need of further analysis is growing stimulating confrontations with further laboratories which faced similar problems with the aim to set up a standard routine analytical method with more reliability.

Available references able to unfortunately do not report interlaboratory studies for asbestos fibres in water, existing references indicate considerable variability (Chopra,1978; Collins et al, 2000), the meanwhile all critical features should be considered such as the natural origin of waters, samples not altering treatments, laboratory possible pollution phenomena, migration processes of thinner fibers etc.

References:

1. CFR 40, Parts 142 and 143. National Primary and Secondary Drinking Water Regulations: Proposed Rule. Federal Register, Vol 54, No P7, May 22, 1989, p. 22062-22160.
2. Collins GB, PW Britton, PJ Clark, KA Brackett, EJ Chatfield. Asbestos in drinking water, performance evaluation studies. Advances in Environmental Measurement Methods for Asbestos. ASTM STP 1342, ME Beard, HL Rook, Eds., American Society for Testing and Materials, 2000.
3. Environmental Protection Agency (EPA), Office of Research and Development. Determination of asbestos structures over 10 µm in length in drinking water, Method 100.2, June 1994.
4. Environmental Protection Agency (EPA). Interim method for determining asbestos in water. EPA-600/4-80-005, Jan 1980.
5. Paoletti L, D Batisti, E Funari. La presenza di amianto nelle acque potabili: alcuni dati sulla situazione italiana. Acqua Aria agosto/settembre 1996: 685-687.
6. Cherubini M, G Fornaciai, F Mantelli, E Chellini, C Sacco. Results of a survey on asbestos fibre contamination of drinking water in Tuscany, Italy. J Water SRT-Aqua 1998, 47 (1): 1-6.
7. Buzio S, G Pesando, GM Zuppi. Hydrogeological study on the presence of asbestos fibres in water of northern Italy. Wat Res 2000, 34 (6): 1817-1822.
8. Chopra KS. Interlaboratory measurements of amphibole and chrysotile fiber concentration in water. J Test Evaluat 1978, 6 (4): 241-247.

ANALYSIS OF ASBESTOS FIBERS IN HAZARDOUS WASTE LANDFILL LEACHATE: THE FALL PROJECT

L. Zamengo¹, S. Polizzi¹, F. Paglietti², S. Malinconico², F. Cappa², P. Luciani³, G. Fasciani⁴

¹ *Physical Chemistry Department, Università Ca' Foscari, Venezia, Italy*

² *ISPESL, Istituto Superiore per la Prevenzione e la Sicurezza sul Lavoro, Roma, Italy*

³ *Barricalla Spa*

⁴ *SGS SpA*

The FALL project (LIFE03 ENV/IT/00323) stems from the need to verify the possible environmental risk that could be generated by the presence of asbestos fibres in landfill leachates, an occurrence already pointed out in a preliminary study carried out in 2001 by the University of Venice in collaboration with ISPESL [1].

The project has three main objectives:

1. to develop a methodology for monitoring asbestos fibres in leachates
2. to monitor the leachates produced by the Barricalla (TO) landfill
3. engineering and construct a prototype plant for filtering asbestos fibres.

The filtering process of asbestos microfibrils needs low porosity filters, which can be easily clogged by the presence of organic matter and other materials dispersed in the leachates. This calls for a treatment to reduce the organic load before filtration. A pre-treatment is also needed for the analytical process, in order to allow the observation of asbestos fibres otherwise embedded into organic matter. The project foresees the experimentation with treatments which could be able to reduce the organic matter load in the leachates.

The key outputs are:

1. the analytical protocol
2. the analytical data obtained from the samples collected at the Barricalla landfill
3. the prototype

The analytical protocol task has been completed. It consists of a collection of procedures for the analytical determination of asbestos fibres in liquids with an high content of organic matter. From sample collection to fibres observation, the most important features for routine analyses with the most used microscopy techniques (MOCF, SEM and TEM) have been investigated and reported. Problems encountered during experimentation have been faced and described and optional modifications to standard procedure discussed.

Monitoring of the landfill is currently in progress. The first year report will be soon available on-line on the project web-site (http://www.unive.it/fall/menu/documents_it.html). By now, a great decrease in the asbestos fibres concentration has been noticed as compared to previous data [1]. This is interpreted as a consequence of the stabilization of the disposed waste and to the capping of the landfill occurred by the last three years. Several titanium-dioxide and other inorganic fibres with an asbestos-like L/D ratio have also been observed during analyses. Both of them are currently counted and separately recorded, so that it will be possible to use them as reference for testing the efficiency of the developed filtering system.

As for the prototype, the construction has been completed. Tests are currently carried out on-site to determine the best fitting for the automation cycle. The treatment is composed of three different steps: a) a 220 µm-filtration, to cut off the organic aggregates usually present in the leachates as sediments; b) an oxidation/heat exchanging step, in which liquids are conveyed into the reactor, mixed with reactants and heated with microwave radiation; c) a set of filters from 25 µm to 0,5 µm, to block all the fibres with dangerous dimensions. While one batch is undergoing the oxidation step, the raw leachate for the following batch is pre-heated by exchanging with the previously treated one and an automation cycle is performed. No sludge has been produced by this sequence and the only waste are the filtering units after their decay.

By the end of the project on December 2006, a final report will be produced and made available on the web site.

[1] F.Paglietti, L.Zamengo, S.Polizzi, G.Fasciani, M.Giangrasso. *Trattamento dei percolati delle discariche per RCA: sperimentazione per una corretta depurazione*. Atti del convegno. L'industria e l'amianto. Roma, CNR (2001).

Session: Exposure monitoring and regional mapping

D. Bard	Personal passive samplers use to monitor the exposure of maintenance workers (industrial plumbers) to asbestos
S. Clarelli	The choice of individual protection devices for asbestos remediation workers
T. Marchi	Professional exposure and environmental pollution during remediation of asbestos-containing materials
M. Guidi	Asbestos remediation in acetylene cylinders
A. Verardo	Informatic system for data analysis and evaluation
L. Amato	Evaluation of the asbestos risk in the alta val Lemme area (Piemonte)
G. Bultrini	Microscopic and microchemical investigations on the fibrous amphiboles from Etna volcano district (Catania-Italy)
A. Gianfagna	Fibrous and asbestos-like minerals in volcanic soils of Biancavilla (Catania): identification, classification and environmental impact assessment
E. Renna	Asbestos containing material mapping of Emilia- Romagna region: application of 18 D.M. 101/2003
B. Sperduto	Environmental pollution from airborne asbestiform fibres: development of fibre propagation maps
L. Fiumi	Mapping of the asbestos-cement by remote sensing and GIS

PERSONAL PASSIVE SAMPLERS USE TO MONITOR THE EXPOSURE OF MAINTENANCE WORKERS (INDUSTRIAL PLUMBERS) TO ASBESTOS

G.Burdett¹, D.Bard¹

Health and Safety Laboratory, Harpur Hill, Buxton SK17 9JN, United Kingdom

Past industrial manufacture and use of asbestos containing products has led to a high incidence of asbestos related diseases and this accounts for a high proportion of all industrially related cancers. The annual mortality rates due to past asbestos exposure are predicted to continue to rise over the next 15 years, regardless of any further controls that could be applied now. Although United Kingdom (UK) and European Union (EU) have taken measures to reduce the risk from asbestos exposure, there are a number of sources that have the potential for continuing exposure and future disease. Large amounts of asbestos are still in place in buildings and epidemiological data suggest that there has been and continues to be a significant risk to demolition and maintenance workers, who may through their work, use or disturb asbestos-containing materials.

The sampling and assessment of maintenance workers' exposure is a particular problem because they may not know that they are working with asbestos containing materials. A strategy to monitor their true exposure has been developed and applied to one group of workers.

The asbestos exposure of industrial plumbers was measured using personal passive samplers developed at the Health and Safety Laboratory (HSL). The light-weight samplers, which collect particles by electrostatic attraction, are simple to use and do not require prior knowledge that asbestos is to be disturbed as does conventional sampling. The samplers, along with activity logs, were issued by post and analysed, after return, using transmission electron microscopy (TEM). The activity logs were used to assess whether maintenance workers were knowingly or unknowingly exposed to airborne asbestos fibres during a course of a working week. The monitoring carried out in parallel with a questionnaire provided a detailed picture of workers' awareness, assumptions and responses to working with asbestos containing materials.

The results of the TEM analysis of the passive samplers showed that the percentage of workers exposed to $>5 \mu\text{m}$ asbestos structures was 62% in round 1 and 58% in round 2. For phase contrast microscopy equivalent (PCME) asbestos fibres, the values were 46% and 29% respectively. The number of workers reporting work with asbestos containing materials (ACMs) on the sample logs were around 20% and half of the plumbers would expect to encounter ACMs only once a year according to their responses from the main questionnaire. These results suggest that the maintenance workers were underestimating or were unaware of their contacts with ACMs during the week sampled.

THE CHOICE OF INDIVIDUAL PROTECTION DEVICES FOR ASBESTOS REMEDIATION WORKERS

S. Clarelli

Presidente di ASSOAMIANTO, www.assoamianto.it

Associazione tra consulenti, operatori nell'ambito della rimozione, smaltimento e bonifica dell'amianto e quanti sensibili alle problematiche ambientali inerenti

Nei lavori ove i rischi legati all'esposizione a fibre d'amianto non possono essere evitati o sufficientemente limitati da misure tecniche di prevenzione o da mezzi di protezione collettiva, il datore di lavoro è tenuto a fornire ai lavoratori idonei D.P.I. per le vie respiratorie o respiratori, opportunamente scelti.

Il criterio guida per la scelta del respiratore è basato sul grado di protezione richiesto in rapporto alla concentrazione di fibre d'amianto aerodisperse.

I respiratori maggiormente utilizzati sono quelli a filtro: l'aria ambiente passa attraverso un filtro il quale, agendo opportunamente sulle fibre d'amianto aerodisperse, rende l'aria stessa idonea alla respirazione.

I respiratori a filtro si distinguono in funzione della tipologia e, per ogni tipo, in base al grado di protezione offerto.

Le norme vigenti fissano i massimi valori ammessi sia per la penetrazione iniziale attraverso i filtri antipolvere (classi P1, P2 e P3) sia per la perdita verso l'interno imputabile al facciale ed eventualmente ad altri componenti. Dando per scontata la presenza di una certa concentrazione di inquinante all'interno del facciale, a tal proposito si definiscono alcuni fattori tipici, vale a dire: fattore di protezione (FP), fattore di protezione nominale (FPN), fattore di protezione operativo (FPO).

Inoltre per i diversi tipi di respiratori, l'Allegato 3 del Decreto del Ministero della Sanità 20 agosto 1999 riporta sia i valori del FPN e quelli del FPO sia la relazione che fornisce il limite massimo di esposizione ad un certo inquinante in funzione del fattore di protezione operativo del respiratore e del valore limite di esposizione adottato per quell'inquinante.

Per lavori di bonifica durante i quali vengono di solito raggiunte concentrazioni elevate di fibre di amianto sono normalmente preferiti gli elettrorespiratori.

Poi, in condizioni di insufficienza di ossigeno o in presenza di livelli di esposizione estremamente elevati, vengono utilizzati i respiratori cosiddetti "isolanti" i quali mettono in comunicazione le vie respiratorie dell'utilizzatore con una sorgente di gas respirabile isolata o esterna, rispetto all'ambiente di lavoro.

Infine, nel caso di lavori di manutenzione o di riparazioni circoscritte, non essendoci un elevato rilascio di fibre, è consentito l'uso di una semimaschera con filtro P3.

In conclusione, le norme definiscono i tipi di Dispositivi di Protezione delle vie respiratorie o respiratori e altresì fissano i gradi di protezione richiesti: la scelta dei respiratori è anche condizionata dal tipo d'intervento di bonifica al quale è associata una data concentrazione di fibre aerodisperse.

PROFESSIONAL EXPOSURE AND ENVIRONMENTAL POLLUTION DURING REMEDIATION OF ASBESTOS-CONTAINING MATERIALS

M. Guidi¹, T. Marchi¹, R. Montagnani¹, G. Magarotto¹

¹Local Health Unit of Venice, Public Health Department Occupational Medicine

In a space of eleven years (1993-2004) we analysed using phase-contrast light microscopy 25.395 air samples taken during remediation of asbestos-containing materials (ACM) at some civil, commercial and industrial sites. The Public Health Laboratory of our Local Health Unit and a few other qualified laboratories performed the analyses: 18.941 were from ambient air sampling (AAS), 6.454 from personal sampling (PS). Different types of remediation were considered: asbestos in a friable matrix (flock asbestos), in buildings of civil or commercial purposes (1.244), friable asbestos insulation on manufacturing (2.932), asbestos in cement matrix of pipelines or thermal fittings that has to be demolished before removing (6.417), removal of compact materials as plates of cement asbestos (9.429) or linoleum (712), removal of materials of intermediary consistence, as fabrics or pressed asbestos (2.566), removal of insulation with the technique of the glove bag (1.322), other activities, such as collection and packaging of wastes and rubbles scattered in industrial areas or fields (773).

The greatest difference from the operational point of view is that the activities of remediation of friable material, of intermediary friability or compact asbestos, even if removed after demolition, have to be done only in a confined site. The communication between the site and the external environment is given by a decontamination unit (D.U.) for workers and materials, with adjacent zones denominated "dirty" and external exit zones denominated "clean". The passage of the personnel and the materials through such Unities must comply with very strict procedures.

Points of collection were as follows : 63,1% of the samples were from the sites, 3,1% from the dirty parts of the D.U., 16,4% from the clean parts of the DU, 17,4% from outside and in proximity of the sites.

The private qualified laboratories that contributed to the collection of data are adopting the quality standards of the suitable analytical determinations in accordance with our national law, both with regards to the methods of sampling and criteria of reading and reporting. For quality purposes the control "on the site" of the methods of sampling and the reliability of the used instrumentation was adopted, together with the reading in double of the most relevant samples.

Both data from the AAS during the operations of remediation and the PS during the same operations, point out clearly that it exists an "on site " enormously different polluting potential, according to the various characteristics of the asbestos material and the type of work done. The most dangerous category seems to be that of remediation on the friable asbestos. In the AAS an average of 448 fibres /litre (F/l) (C.L. 326-570) and in the in PS an average of 2.008 F/l (C.L. 1.390-2.627) were found.

A relevant pollution is also caused by the remediation on friable asbestos at industrial premises, even if lower than the former one (AAS. 291 F/l, C.L.248-335.; C.P. 1.012 F/l, C.L.816-1.207). Insulation materials too can cause a considerable risk; levels of pollution higher than 100 F/l, in the case of remediation with demolition, as in the case of remediation of the covers of pipelines (AAS. 68 F/l.C.L.52-83; C.P. 135 F/l.C.L.116-154) were found.

The remediation on asbestos in medium-friable matrix, as the pressed asbestos or fabrics, both by AAS and by PS were found to cause asbestos pollution at a level much lower than the limit of action of 100 F/l (AAS. 6 F/l, C.L.5-8; C.P. 6 F/l, C.L.5-7). We couldn't anyway determine the influence of the confinement and of the indoor air exchange on this low exposure at the site. As a matter of fact, less polluting work activities are always characterized by exposures much lower than the level of action, despite the remediation is developed without confinement.

These can be considered as very low risk activities. The removal of plates of cement asbestos (AAS. 12 f/l C.L.10-14; C.P. 14 F/l.C.L.12-16), the removal of linoleum (AAS 2 F/l (C.L. 2-3); C.P. 3 F/l (C.L.2-3), the removal of insulation performed with the technique of the glove-bag (AAS 5 F/ (C.L.3-8); C.P. 6 F/l (C.L.5-7) must be included among these low risk activities.

On the basis of our data, four homogeneous subsets come out: low exposure (linoleum, glove bag, pressed, fabrics and plates of cement asbestos), medium exposure (pipes of cement asbestos), high exposure (friable industrial), very high exposure (flock asbestos), (analysis of the variance, Scheffe's test for $\alpha = 0,05$).

The techniques and the procedures of confinement seem to be adequate to take care of the surrounding environment even during the most demanding remediation, such as those of asbestos in friable matrix. In fact, when during the phases of remediation in the sites high levels of environmental pollution were reached (321 F/l.C.L.278-363), they were much lower in the dirty DU (45 F/l C.L.31-58) and even more in the clean DU (8 F/l C.L.5-12) and very low levels of pollution were measured in the adjacent zones (4 F/l.C.L.3-5).

Analysing data of PS according to the different tasks it comes out that in demolitions of friable asbestos levels of exposure were very high (1.403 F/l C.L.1.138-1.669), the same applies to the operations of packaging of wastes and removal of insulation (2.301 F/l.C.L.1.622-2.982). In the activities of aspiration of dusts, the average exposure was higher than the action level (202 F/l.C.L.26-377). Lower levels of pollution are measured during the " wetted cleaning" (80 F/l.C.L.9-151) and the collection of materials at the site (40 F/l.C.L.15-66).

During the demolitions of compact asbestos pipelines, as it has been said already, levels of pollution higher than the level of action were found, but much lower than those found in the case of remediation of the friable ones : high levels of exposure were found only during the demolition (505 F/l.C.L.431-579) and the packaging (388 F/l.C.L.284-493);

levels during the "dry aspiration " were low (72 F/I C.L.10-133), even lower during the collection of materials (55 F/I, C.L.40-70) and in the wetted operations (49 F/I, C.L.28-71).

During the activities of removal of plates of cement asbestos, the analytical values are always very lower than the limit of action of 100 F/I: removal of the plates (11 F/I, C.L.9-12), packaging (14 F/I, C.L.9-18), treatment of the surfaces of the plates with "lock down" agents (9 F/I.C.L.4-14), aspiration (4 F/I.C.L.3-4), collection of materials (3 F/I.C.L.3-4).

The efficiency of the safety procedures, the systems of confinement, the techniques of cleaning of the sites of remediation is evident both from the concentrations at the site before the remediation (3 F/I.C.L.2-3) and those verifiable at the end of the work (3 F/I.C.L.2-4), which are always lower than the limit of exposure for the population at large (20 F/I). Along the years of observation, analyses performed during the remediation ACM in friable matrix (in buildings and at industrial premises) show a very discontinuous trend, with a clear tendency to the reduction of levels of exposure starting from the year 2000. The remediation on compact ACM made friable by the techniques under use (cement asbestos that dresses pipelines and thermal or industrial fittings) show an irregular and discontinuous trend, with a certain tendency to the increase of the exposure in the last 6 years. The remediation on compact ACM (plates of cement and linoleum) shows instead a definite increase of the levels of exposure starting from the year 2000. Such increase is significant, even if of less amplitude for the materials of intermediary friability (fabrics or pressed).

We also made a comparison of the data of AAS during the phases of remediation in two six -years periods (1993 to 1998 and 1999 to 2004). For the first period, we noticed a generalized reduction of the level of environmental pollution, especially relevant and statistically significant in the more polluting activities, such as the remediation of flock asbestos, friable industrial, pressed asbestos or fabrics, covering of pipelines or thermal fittings. Also the removal of plates of cement asbestos shows a significant reduction of the levels of exposure.

Data from PS confirm this positive trend, that is very clear for the remediation of friable materials. The tendency to the reduction of the asbestos air pollution during the activities of remediation of ACM applies in a generalized way to the whole range of work duties, particularly to those with great polluting potential, without considering the friability of the material.

On the contrary, for the activities of remediation of the cement asbestos of pipes of thermal or industrial fittings, especially in the activities of demolition, but also those of collection, in the recent years higher levels of asbestos pollution were measured at the sites

Conclusions

The polluting potential of the remediation of ACM, from the point of view of the air availability of breathable fibres, depends on the friability of the matrix, with a huge variation between the friable material and those that are compact. The compact ones can be a danger only in the case that the remediation has to be done with demolition, as for instance in the case of the covering of pipelines or thermal fittings. From the point of view of the polluting potential from our data four homogeneous subsets come out: low exposure (linoleum, glove bag, pressed, fabrics and plates of cement asbestos), medium exposure (pipes of cement asbestos), high exposure (friable industrial), very high exposure (flock asbestos). The operational procedures and the techniques of confinement during the remediation, seem adequate to protect the surrounding environment.

The low exposures found in the activities of non demolition removal of compact materials when correct procedures of work are used allow means of prevention less demanding for the companies, while still keeping a low environmental impact.

The reduction of levels of environmental pollution, particularly evident in the most polluting activities testifies of an increasing improvement of the techniques of remediation. Particularly, the use of more and more sophisticated and manageable depression tools and aspirators for solid and liquid substances guarantees an effective air exchange at the sites, even in the very narrow spaces that are typical of the remediation of industrial fittings. The use of "lock down" agents with great capacity of penetration in the materials to be removed determines a low level of air concentration of breathable fibres in all operational phases. Eventually the better control of the microclimate, formerly very uncomfortable in summer in many cases of remediation, allows workers' longer times of permanence within the confined zone, with better opportunities for a proper planning of activities.

References

Proceedings of the National Conference "Malignant Mesothelioma, occupational and non occupational exposures to asbestos." Pisa, November 13-14 th 1990, pp. 222-226.

Magarotto G., D'Andrea, F., Guidi M., Ferraro P. (edited by). Asbestos. Health problems within living and work environments. Region of Veneto, 1993, pp. 71-90.

Maino A., Gianelle V., Onida F., Albiero S. Exposure to asbestos in operations of removal or conservative treatment of coverages in eternit. Med. Lav., 86, 546-554, 1995.

Region of Emilia Romagna. Asbestos: removal, disposal and control. Material, 1992.

Wilmoth R. C., Taylor M.S., Meyer B.E. Asbestos release from the demolition of two schools in Fairbanks, Alaska. Appl. Occup. Environ. Hyg., 9, 409-417, 1994.

ASBESTOS REMEDIATION IN ACETYLENE CYLINDERS

Massimo Guidi¹, Nicola Cirino², Michela Vicario³, Alessandro Trovarelli³

¹ *Dipartimento di Prevenzione, ASL 12 Veneziana – SPISAL, Piazzale S. Lorenzo Giustiniani 11/D, 30175 Mestre-Venezia, Italy*

² *Studio di Ingegneria Ambientale, via Gruppo Conegliano 26, 31100 Treviso, Italy*

³ *Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, 33100 Udine, Italy*

Acetylene is widely used in oxy-acetylene torches for welding and cutting of metals and in several other applications. Under industrial practice it is stored in steel cylinders under pressure. The cylinders are filled with a porous material that contains a solvent, usually acetone, in which acetylene is soluble. The porous material is constituted by a capillary system of interconnecting micropores and typically contains calcium silicate, water and additives to improve mechanical and crushing strength and other properties. Up to early '90s a reinforcing fibre such as asbestos, was added to the formulation of the filler. Today this use is forbidden, but the disposal of old products has given rise to considerable problems relating to occupational hygiene. This is because there is a great amount of asbestos in discarded storage cylinders for acetylene welding gas, that explains why asbestos has proved a complicated problem when old acetylene cylinders are taken down or dismantled. In addition to solid waste, discarded acetylene cylinders contains residual acetone (a few litres) which could otherwise leach into the environment upon disposal of the cylinder. Moreover, on site storage of hazardous waste also constitutes a violation of the environmental protection laws. Thus, there is a strong need to develop an economically attractive and effective system of treating acetylene cylinders in order to remove the residual acetone from exhausted acetylene cylinders before treating of the solid filler mass for neutralizing asbestos containing waste.

In this work we have studied a system for the remediation of acetylene cylinders by (i) recovery of acetone, and (ii) separation and neutralization of the porous adsorbent containing asbestos. The first step is carried out by heating of the acetylene cylinders in a desorption unit, where the cylinder reaches the temperature range 70-85°C for a period of 6-8 hours and collecting the solvent in a condenser unit. A decrease of desorption times can be reached by operating at reduced pressures or by using a carrier gas like nitrogen in adsorption/desorption cycles. When operating under reduced pressure a vacuum pump is positioned after the condenser unit in order to facilitate the generation of reduced pressure. Once the solvent recovery has been completed the cylinders are forwarded to a shell cutting section. The purity of acetone solvent recovered (97%) is affected by the presence of residual acetylene and other organics, mostly reaction products deriving from condensation of acetone. The efficiency of the desorption process has been tested by analysis of the filler that has been subjected to laboratory TG-MS analysis in order to detect the presence of residual solvent. There is a strong effect of reaction time and temperature on the quantity of acetone that is recovered, which is almost quantitative after 8 hours at 85°C.

After recovery of acetone the cylinder is safely cut in two using a lathe and obtaining two open cylinders. The recovery of internal filler is facilitated by utilizing a driller machine and by finely grinding the porous matrix. The dust is collected in a big bag which is then disposed in authorized plants. The recovery of metal is carried out after cleaning of the empty cylinders from residual material.

Acknowledgements: We thank SFA srl for financial support.

INFORMATIC SYSTEM FOR DATA ANALYSIS AND EVALUATION

Alberto Verardo

Regione Liguria Servizio Prevenzione

All'interno dei Piani Regionali Amianto, la conoscenza del rischio è rappresentata dalla individuazione e dalla conseguente valutazione dei manufatti contenenti amianto installati in edifici ed impianti.

Tale consapevolezza ha trovato, per la quasi totalità dei casi, riscontro nella produzione di schede di notifica predisposte per il censimento che i singoli detentori e responsabili per la gestione della presenza compilano e producono indicando la localizzazione della presenza, determinandone la tipologia, evidenziandone le condizioni.

Dalla constatazione delle condizioni di conservazione se ne ricavano le dovute indicazioni per le conseguenti azioni di bonifica, se ed in quanto necessarie. L'efficacia di tale constatazione ha però valore se viene ad essere effettivamente ed oggettivamente definita la condizione che sancisce l'esigenza di intervento e non rende ininfluente se non proprio disattendente quanto viene dichiarato.

Ne consegue l'esigenza e l'urgenza di disporre di adeguati strumenti che consentano di raccogliere tutti gli elementi di oggettività possibili e permettano di definire lo stato di conservazione del manufatto in funzione dell'adozione delle opportune misure di salvaguardia.

La realizzazione e l'impiego di adeguati strumenti è in linea con le esigenze di controllo e verifica che le Regioni devono promuovere assicurando la massima oggettività possibile consapevole delle problematiche sanitarie che la presenza di manufatti contenenti amianto può determinare nel caso di rilascio di fibre.

La rilevante e diversificata presenza di manufatti con amianto in edifici (civili, industriali, rurali ed agricoli) ed impianti presenti in Liguria è testimoniata dall'elevatissimo numero di prodotti commercializzati che si sono, nel tempo, spalmati in tutte le realtà seppure con differente incidenza e connotazione.

Lo strumento informatico elaborato dalla Regione Liguria è partito dall'esame dei contenuti delle schede di autonotifica che progressivamente sono state inserite nel sistema rendendole compatibili attraverso una pulitura del dato ed una omogeneizzazione dello stesso.

Il coacervo dei dati, pervenuti attraverso informazione cartacea, è stato informatizzato dopo una operazione di pulizia che ne ha reso possibile l'utilizzo ed ha dato vita ad un sistema anagrafico regionale amianto che rappresenta un data base relazionale opportunamente sviluppato.

Da esso sarà possibile trasferire e ricevere, con opportune limitazioni legate al rispetto delle normative connesse all'applicazione della privacy e di quant'altro dovuto, dati, dialogando con le ASL del territorio regionale.

Il funzionamento prevede l'inserimento degli elementi caratterizzanti all'interno di una specifica maschera identificativa della localizzazione del manufatto che viene notificato, che trasferisce i medesimi in altri ambiti di collocazione per consentirne l'ampliamento e lo sviluppo.

Le funzionalità informatizzate risultano la gestione completa dei dati edificio, la gestione dei dati relativi alle matrici compatte e friabili notificate, la gestione dei dati relativi ai soggetti coinvolti, la gestione dei dati relativi alle società, agli enti, ai condomini (nel caso di edifici di civile abitazione), con possibilità di elaborazioni rese disponibili in forma raggruppata per soggetto, tipologia di organismo, comune di ubicazione della struttura/impianto e tipologia di materiale.

Il sistema storicizza il dato inserito ed attraverso opportune maschere di completamento consente l'inserimento dei dati aggiornati connessi alla produzione periodica delle schede riguardanti lo stato di conservazione del materiale.

Il sistema punta all'analisi, tramite algoritmi applicati ai dati inseriti, dello stato di degrado del manufatto per acquisire le informazioni necessarie a decidere gli interventi opportuni da compiere, disponendo di tutte le potenzialità necessarie.

L'operazione di valutazione dell'esistente e la conseguente espressione di giudizio può far giungere alla determinazione di dover operare una bonifica per rimozione del manufatto installato in quanto il medesimo può determinare rilascio di fibre.

EVALUATION OF THE ASBESTOS RISK IN THE ALTA VAL LEMME AREA - A RESEARCH PROJECT PROMOTED BY PROVINCIA DI ALESSANDRIA - DIREZIONE AMBIENTE E TERRITORIO

L. Amato¹, M. Ferrarotti¹, C. Piccini², E. Carraro³

¹ *Provincia di Alessandria*

² *Arpa – S.C. 16 prevenzione del rischio geologico della Provincia di Alessandria*

³ *Università del Piemonte Orientale Amedeo Avogadro*

INTRODUCTION

From the geological point of view, the presence of rocks containing asbestos in the southern zone of the Alessandria Province, is since long time known.

Recently, in the area of Alta Val Lemme, interested by important plans of development and infrastructures, the problem of natural presence of asbestos minerals has risen in important way; therefore, the Province of Alessandria, Directorate Environment and Territory, has started a research project in order to map natural presence of asbestos, and to define the linked characteristics of risk.

The surveying area is placed along the tectonic limit between the Voltri Group and the Sestri-Voltaggio Zone, known as Sestri-Voltaggio Line.

The Sestri-Voltaggio Zone is composed by three tectonic units which differ for paleogeographic pertinence and/or metamorphic features: the Trias-Lias Unit prevailing carbonate succession of drawing continental margin, the Cravasco-Voltaggio Unit an ophiolitic succession, and the Monte Figogna Unit. At least, going from Voltaggio to Carrosio outcrop the Conglomeratic complex and Mudstones of Tertiary Sedimentary Piedmont Basin.

The interesting outcrops for this study are represented by serpentinites, frequently found in ophiolitic bodies and the terziary covers deriving from their delay, in which occurs asbestos minerals.

1. The territory

Situated in the south of Piemonte region, in Province of Alessandria, along the boundary with Liguria region. Included in heights between 250 mt. and 1100 mt. ,it's a low urbanized area with mostly agricultural and tourist vocation. It involves the inhabited centres of Voltaggio, Carrosio and Fraconalto.

The surveying area is placed along the tectonic limit between the Voltri Group and the Sestri-Voltaggio Zone, known as Sestri-Voltaggio Line.

The Sestri-Voltaggio Zone is composed by three tectonic units which differ for paleogeographic pertinence and/or metamorphic features: the Trias-Lias Unit prevailing carbonate succession of drawing continental margin, the Cravasco-Voltaggio Unit an ophiolitic succession, and the Monte Figogna Unit. At least, going from Voltaggio to Carrosio outcrop the Conglomeratic complex and Mudstones of Tertiary Sedimentary Piedmont Basin.

The interesting outcrops for this study are represented by serpentinites, frequently found in ophiolitic bodies and the tertiary covers deriving from their delay, in which occurs asbestos minerals.

2. Sample collection

The first phase of study has carried out a geological survey on the territory, for the definition of the areas where taking out soil and substrate samples, considering not only ophiolitic outcrops, but also the tertiary covers deriving from their delay.

Contextually a meteoroclimatic study has been realized, for the identification of the driest periods of the year and therefore more representative from the point of view of fibres dispersion and for the identification of the main directions of winds.

Once geologic and meteoroclimatic data have been processed, and once identified the areas and the period of the year which represent the worst case according to risk of fibre dispersion, a monitoring of the air quality in 11 emplacements chosen on the base of the outcomes of the meteoroclimatic study, 6 surface water sample in correspondence of the main confluences of the main rivers and streams, and 33 samples of soil (cover and substrate), have been made.

To achieve statistically manageable data, the starting step has been the division of the interested area in 11 quadrants surfacing each mt. 250x250. From each quadrant were collected 3 soil samples and was placed a station for the monitoring of atmosphere quality.

The analysis on soil samples have confirmed the presence of a moderate level of asbestos (around 1/3 of the examined samples) both in the ophiolitic Units (4 samples above 10) and in the covers (6 samples above 10), witnessing an ordinary situation which is largely distributed on all the Alps chain.

As everyone knows, the risks caused by the presence of asbestos fibres in the environment are due to their dispersion in the atmosphere, specially if involved by the wind.

In the faced study, it hasn't been revealed a correlation between the existence of asbestos fibres in the soil and their dispersion in the atmosphere (there were only two cases which found the presence of fibres, probably from anthropic origin).

The analysis on water samples (carried out only at a knowledge-scope level) have obtained values very far (max 71 f/l) from the minimum limit of 100.000 f/l (Kanarek 1989).

At this point the question was if it could be possible to affirm the existence of a real natural asbestos risk in Val Lemme and, if so, if it could be tempted a first assessment.

3. Hazard identification and estimation of geological risk.

First of all, it has been identified the site conceptual model, from which were extracted the sources (Cataclastic and tectonic serpentinites rocks), the pathways (air and water), the exposure factors (drinking water ingestion, soil ingestion, inhalation) and the receptors (resident population, workers and tourists).

The second step was realized by integrating the analytical data with the information provided by the site conceptual model, obtaining by this way the definition of the danger and successively of the risk.

This type of approach registered a very easy utilisation, but permitted at the same time to obtain an immediate risk estimation starting from geological dangerous data.

4. The epidemiological study

To achieve information on Alta Val Lemme population health conditions related to the natural environmental asbestos exposure risk, it has been conducted an epidemiological research.

With this aim it has been realized a descriptive epidemiological study with geographical analysis to identify possible pathologies or mortality cluster reliable to the environmental asbestos exposition in the area of Alta Val Lemme.

This study has been conducted comparing the values of some demographic and sanitary contest of the Alta Val Lemme population with those of Alta Val Borbera population, in which area environmental asbestos is absent. Successively, the values obtained from the two populations have been compared with those of the Piemonte region population. From the research emerges a health condition similar to the Alta Val Borbera mountain population and for some aspects even better than that of the regional one.

At last, for what concern the starting hypothesis of the research, it doesn't appear any health problem related to an asbestos exposition naturally present in the environment.

In conclusion then it may be suggested, obviously, assumed the risk condition due to the exposition to environmental asbestos, to apply all necessary safety measures both to workers and to residents before beginning any excavation and ground removal intervention.

CONCLUSIONS

From this study it has been possible to deduct that for the analyzed area the asbestos fibre concentrations found in the environmental matrices, are always under the amount allowed by law and guidelines of ISS.

From the geological - environmental risk analysis, turns out that the risk for resident population and for occasional visitors deriving from the asbestos presence in natural shape, can be thought acceptable.

It emerged besides that the results obtained from the epidemiological study and from the geological environmental analysis are comparable. It may be now interesting verify the validity of this last type of analysis applying it to some other sites.

If its validity should be confirmed, we believe that, for its facility of use, it could easily be a liable tool to face first level risk analysis in other Italian and abroad sites, where the existence of natural asbestos represents an environmental problem.

For what concerns the popularization of the results, we must always take in mind that when we face audience, media and non specialized partners, it is often insufficient the simple technical communication of events relied to the safety and the probability of harmful events, specially if compared to the need of reduce disinformation and quiet the risk (both real or just perceived).

The result is that, with the aim of satisfy the requirements of a complex society, a modern approach towards the risk management cannot ignore irrational and subjective perceptions, and for the same reasons must carefully consider the psychological and sociological factors.

It is then necessary to complete the essential technical-scientific approach with a careful view towards public relations (Oboni, Oldendorff 1997).

The support to this integration must not carry to the banalisation of citizen doubts and fears by mind at rest behaviours (which before or after are counterproductive for everyone). At the opposite it must correspond to the need of facing an increased sensitivity in relation to the qualitative and quantitative level of the questions lifted by the civil society, specially referring to the project emotively, socially and environmentally most impacting.

MICROSCOPIC AND MICROCHEMICAL INVESTIGATIONS ON THE FIBROUS AMPHIBOLES FROM ETNA VOLCANO DISTRICT (Catania-Italy)

G. Bulttrini¹, E. Ciliberto¹, L. Fragalà¹, G.Miretto¹, P. Plescia²

¹ *Dipartimento di Scienze Chimiche Università di Catania, viale A.Doria 6, 95125 Catania Italy*

² *CNR Istituto per lo Studio dei Materiali Nanostrutturati - Area della Ricerca RM1 Montelibretti (RM)*

In the Town of Biancavilla (Catania), the occurrence of a fibrous amphibole that has the characteristics and pathogenicities of amphibole asbestos is well known(1,2). Such phase, identified as Fluor – edenites (1), has been found in a rather common volcanic formation in SW of Etna volcanic district. Consequently, it is necessary to understand the aspects of formation of these amphiboles of Biancavilla, its paragenesis, and the entity of the area interested by its presence. From the data of sampling of the air near Biancavilla, some Authors have found fibers that show the composition of fluorine-amphibole of Biancavilla (3). In the massive materials of the Monte Calvario quarry (the first places where F-amphiboles were founded) it is easy to observe some different kinds of prismatic and acicular crystals with compositions that come from pyroxene to F-amphibole.

Mineralogical and geological data

Acicular, yellow light crystal, now recognized as Fluor edenite, has been discovered for the first time by G. Platania (4) in Contrada Reitana, neighbor to the Town of Acicatena, approximately 25 km from Monte Calvario, Biancavilla. In Reitana the Author discovered this mineral, which he called "Xiphonite", and classified it as a new variety of amphibole for its optical characteristics; in particular Platania described the "Xiphonite" like "crystals of two millimeter, limpid and transparent, of a light to a honey yellow color". They were found inside the cavities in the scoraceous lavas, rich in augite and hematite crystals. In the area there are some benmoreitic lavas, marked in the Geologic map of the Etna Mount like Lpr and Lpd (5), as that in the area of Biancavilla. It's important to note that G. Platania had found those xiphonite crystals grown on the pyroxene surface. It is interesting that the areas where fluor-edenite and "xiphonite" have been found are placed on some faults, and in particular the area of Monte Calvario is placed between two fault systems with NE-SW and N-S orientations, while the area of Reitana is found on one fault with NNE- SSW orientation. Similar faults are disposed in the North-western area and south east of the Etna basin.

Experimental

The mineral samples for analyses have been selected from many samples taken in various places:

- massive samples from Monte Calvario (Biancavilla)
- drilling cut samples from railway line
- airborne fibers .

In the massive samples almost four tipology of crystals can be recognized:

- 1- acicular or prismatic crystals, of transparent yellow or honey, not altered, classified as F-edenite
- 2- prismatic crystals, opaques, orange or red orange
- 3- prismatic crystals of opaque dark orange, classified like "pyroxenes"
- 4- prismatic crystals of opaque black color

All the samples have been analysed by means of X-ray powder diffractometry (XRD), scanning electron microscopy with EDS analyser (SEM-EDS), thermal analyser (DTA-TGA) and optical fluorescence microscopy (OM). The yellow acicular and transparent crystals, analysed in microanalysis, have shown one comparable composition with the F-edenite described by Gianfagna (1). The crystals are transparent but rich of inclusions of dark color. The fibers are rare: they tend to detach from the prismatic crystals. The XRD and SEM-EDS analyses of yellow and honey-coloured crystals confirm the F-edenite composition. The second type is orange, opaque acicular and prismatic crystals. The crystal shape is a prism, tabular, strongly corroded and, to the microcrystal margins, often rich in yellow honey acicular crystals. Also these crystals are F-edenite, but in pseudomorphoses with a lot of pyroxene inclusions. A third type is constituted by dark, cracked orange crystals. Such crystals are common, together with feldspar and fluoro-apatite. Such crystals are Fe-enstatitic pyroxenes covered of an orange layer of approximately 5-20 microns, formed by Fe hydroxides and microcrystalline hematite. In these crystals, F-edenite are crystallised on the pyroxenes surfaces, as dark tabular crystals. Finally, the fourth type are dark-tawny red color crystals in association with augite and magnetite. The F-edenite crystals have been analyzed regarding the residual stress. This analysis was performed by the "two peaks" method in comparison with a stress-free standard, that was a fluor edenite heated at 1000°C for 12 hours. In this way, main peaks of yellow, red and dark F-edenites show that the residual stress is tensile and ranges from 0.1 to 5.5 %. The preliminary data allow to make some hypothesis on the origin of F-edenite and on the spread mechanism that has brought to the dissemination of these crystals on volcanic products, not only in the Biancavilla areas but in many areas of the SW margin of Etna basin. The origin of the fluor-edenite appears to be provoked by hydrothermal convoys, rich in F, subsequent to the formation of faults that cut the volcanic products on SW areas. Such origin and the data on the occurrence of this mineral suggest a fast crystallization in anhydrous conditions and fluorine presence, similarly to what happens in the diffuse crystallization of "wiskers" of fluor amphiboles in some glass ceramics (6, 7). Other Authors have demonstrated that F-edenite can be crystallize from an alkaline silica glass rich in fluorine (8), together with F- phlogopite and clinopyroxene and plagioclase, the same paragenesis that can be seen in Biancavilla samples. The produced crystals therefore are diffuse in statistical way within the glass matrix and show some typical streaks for the acicular fiber separation from the body of the crystal. In conclusion, the following considerations result from the data obtained:

- the F-edenite fibers are formed in anhydrous atmosphere, as a result of a strong localized heating, in presence of fluorine minerals as F-Phlogopite, previously crystallized
- the spread of the fibers is wide. Its spread in air is easy, due to the fibers detach from prismatic crystals for simple mechanical pressure
- the residual stress inside on the F-edenite crystals play a particularly role on the fibers diffusion: infact, the high level of residual stress induces the "explosions" of F-edenite crystals during its simple manipulation

- [1] A. Gianfagna, Paoletti L., Ventura P. *Plinius (Suppl. Eur. Journal of Mineralogy)*, 18, 117-119 (1997)
[2] Paoletti L., Batisti D., Bruno C., Di Paola M., Gianfagna A., Nesti M., Comba P. *Archives of Environmental Health* 55(6), 392-398 (2004)
[3] De Nardo P., Bruni B., Paoletti L., Pasetto R., Siriani B. *Science of Total Environment* 325, 51-58 (2004)
[4] Platania G. *Atti e Rendiconti dell'Accademia di Sc. Lett. ed Arti dei Zelanti, Acireale, Nuova Serie*, Vol. V, pag. 55 (1893)
[5] AA.VV. *Memorie della Società Geologica Italiana Vol. XXIII Romolo Romano editor, (1982)*
[6] Beall G.H., Verres *Refract.* 32 (4), 517-522 (1978)
[7] Beall G.H., *Proc. VII Symp. on Crystallization in Glasses and Liquids*, Sheffield, 6-9 July 2003
[8] Oberti R., Hawthorne F.C. *Raudsepp M. Eur. Journal of Mineralogy*, n.1, pp. 115-122 (1997)

FIBROUS AND ASBESTOS-LIKE MINERALS IN THE VOLCANIC AREA OF BIANCAVILLA (CATANIA, SICILY, ITALY): IDENTIFICATION, CLASSIFICATION AND ENVIRONMENTAL IMPACT ASSESSMENT

A. Gianfagna¹, B. Bruni², S. Mazzioti-Tagliani¹, A. Pacella¹, L. Paoletti²

¹ *Dipartimento di Scienze della Terra, Università degli Studi di Roma "La Sapienza", P.le A. Moro, 5 – 00185 Roma*

² *Dipartimento Tecnologie e Salute, Istituto Superiore di Sanità, V.le Regina Elena 299 - 00161 Roma*

Introduction

Cases of environmental pollution by mineral fibres not classified as asbestos are becoming more frequent, in Italy and in foreign countries. The recent Italian case of Biancavilla is known also to the international scientific community by the way it came about. This is a typical example of non-occupational exposure of an environmental nature caused by natural fluoro-edenite fibrous amphiboles [1], [2]. Although these fibres do not belong to the asbestos group, they are considered the cause of the pleural mesothelioma in this locality [3]. In fact, the Emergency Plan for making in safe of the Biancavilla Site of National Interest (Ministry Decree of 18.7.2002; Official Gazette no.231 of 2.10.2002) was drawn up on the basis of regulations governed by law 471/99 on asbestos-contaminated sites, despite the non-inclusion of the new mineral fluoro-edenite among the five amphiboles referred to as "asbestos". Since 1997 the Department of Earth Sciences of

Rome's "La Sapienza" University, in collaboration with the Higher Institute of Health, has realised the importance of investigating the whole volcanic area of Biancavilla from a geo-mineralogical and environmental perspective.

The aim of this work is to obtain useful information on the areal spreading of these natural fibres and on their morphological, chemical and structural features, directly connected to the presence of the oncological pathologies in the area. The first occurrence of amphibolic fibres in the altered and incoherent lavic products of the Monte Calvario quarries [4] marked a starting point for the investigations of an interdisciplinary nature. These studies aimed to understand and solve the interesting and complex problem of Biancavilla. The finding of fluoro-edenite fibres in the parenchima of an inhabitant woman from Biancavilla who died of a pleural mesothelioma [5] and the recent positive results of toxicological studies, *in vitro* [6] and *in vivo* on rats [7] confirm that exposure to these fibres was the cause of the pleural mesothelioma observed in the local population over the last few years.

Identification and classification of the fibres

Mineralogical and crystal-chemical investigations on the amphibolic asbestiform fibres of Biancavilla have so far been performed through specific methodologies (SEM-EDS, TEM-EDS, XRD, FT-IR, Mössbauer, Raman). The results obtained indicate a composition and a crystal structure of the fibres related to prismatic fluoro-edenite, found for the first time in the same volcanic materials of Monte Calvario and previously studied [1]. Nevertheless, some typologies of fibres would also seem to show tremolitic, winchitic and richteritic compositions, owing to a modest chemical variability present on the inside (Fig. 1).

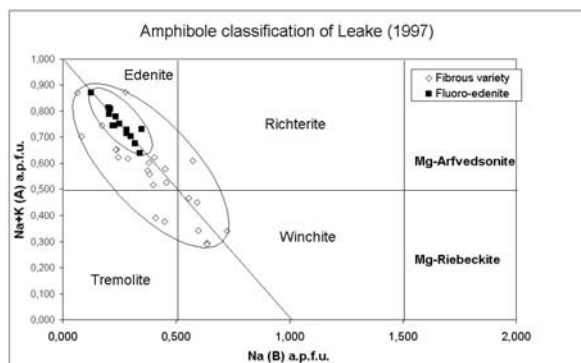


Figure 1 - Classification of the amphiboles from Biancavilla.

enrichment of the amphibolic fibres with respect to the material host to lead specific spectroscopic investigations (XRD, IR, Mössbauer, Raman). This material includes a complex mineralogical association mainly composed of microcrystals of alkali-feldspars, clino- and ortho-pyroxenes, fluoro-apatite, and Fe-Ti oxides. A gravimetric sedimentation method was used for the fine material, exploiting both the different mineral densities and their relevant morphologies. This method allowed obtaining a fibrous material with up to 95% of the amphibolic fibre content.

X-ray investigations enabled emphasizing some differences in the values of the cell parameters. In particular, the a parameter shows a range from 9.84 Å, for the prismatic fluoro-edenite, to 9.81 Å for the fibrous variety, with a resulting reduction of the volume V of the unit cell (901 Å³). This evidence is in good agreement with the chemical variations observed in the fibres; in particular, the Ca and Mg contents are lower with respect to the prismatic fluoro-edenite and they influence the structural dimensions of the B and C sites that contain them.

⁵⁷Fe-Mössbauer spectroscopy allowed checking that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of the prismatic fluoro-edenite is different from the value for asbestiform fibres. There is a higher Fe^{3+} content (over 90%) in the former as against a lower content of Fe^{3+} (over 50%) in the latter. Besides from a mineralogical and crystal-chemical point of view, these results become very important when related to the dangerousness of the fibres for their total Fe content, as well as the Fe oxidation state. A greater Fe^{2+} content associated with the typical asbestiform morphology significantly confirms the hypothesis that the fluoro-edenite amphibolic fibres were really the cause of the mesothelioma in the Biancavilla area.

Last but not least, the preliminary results of the TEM and Raman investigations on the Biancavilla fibres showed a good validity for their specific determinations. TEM, carried out at the Department of Mineralogical and Petrological Sciences of Turin University, enabled emphasizing the particular morphologies of these fibres, never seen with the sole use of SEM. Moreover, through the SAED images, TEM allowed verifying the excellent crystalline quality of the single fibres and their good resistance to the electron beam during the analysis [8]. Raman spectroscopy was carried out at the Department of Environmental and Life Sciences of the University of Eastern Piedmont at Alessandria, and was extremely efficient in the discrimination of the amphibolic fibres from Biancavilla, not only among the fibres themselves but also with respect to the other fibres belonging to the asbestos group [9].

The mineralogical and crystal-chemical investigations performed on these particular amphibolic fibres allowed highlighting a different compositional range. In this way, it is very complicated to make a definitive definition and classification of them, also because these minerals are new discoveries and thus not included in the asbestos list.

In this specific case we used Leake's classification [10], which allows defining the amphiboles on the basis of Na and K contents in the A and B structural sites. Some representative compositional points fall in the fields of already known amphiboles (Fig. 1), and some of them are also included in the asbestos list, like tremolite. Therefore, it is necessary to

conduct a further detailed statistical analysis of the different possible compositions of all the amphibolic fibres from Biancavilla. The aim is to better define and frame them within the environmental health-social problem of the studied locality. The correct definition and classification of the amphibolic fibres, and their relevant crystal-chemical knowledge, may be able to achieve such goal.

Environmental impact assessment.

Subsequent to the preliminary epidemiological investigations in the area of Biancavilla, the environmental investigations allowed relating particular situations not always correlable with human activities. In the specific case at issue, human activities represented only a marginal and indirect role in the local problem, while the main cause lies in a specific natural and environmental context. The compositional differences observed for the fibres found in the building materials, in the aeral-spread particulate, and in the pulmonary parenchima of the deceased pleural mesotelioma victim, fall in the compositional ranges found for natural fibres sampled in the original volcanic products (quarries and environs). Crystal-chemical investigation are in progress on amphibolic fibres sampled in other sites of the whole area of Biancavilla and in neighboring areas having the same geo-mineralogical characteristics of Monte Calvario. These areas have similar geological formations and contain fluoro-edenite fibres. Therefore, the possibility of finding the mineral scattered over other "non-suspect" natural areas is more likely, with a high risk of diffusion.

A recent study on the spread and dispersion of amphibolic fibres in the locality and surroundings of Biancavilla [11] warns of the future risk to the local population that is constantly exposed to this type of mineral fibre not for any occupational reasons. In fact, in the whole territory the spread of the fibres is due to natural factors, such as the climate, and to human ones, such as agricultural activities on contaminated soil, uncontrolled mining activities and unmonitored ground movements.

The investigations in progress in the different sectors of the scientific research (geology, chemistry, epidemiology, biology, medicine) aim to understand and identify the mechanisms that initially caused the high dispersion of the amphibolic fibres in the area. Even if, to date, the intense mining activity of the past seems to be the main cause of the dispersal of these fibres in the area of Biancavilla, the fact that another factor may have greatly contributed to the phenomenon cannot be ruled out. To this end, the fact that particular activities of the past (such as agriculture) on soils containing abundant quantities of amphibolic fibres may have contributed to fibre dispersal in soils even far from the Monte Calvario quarry must be taken into serious consideration.

References

- [1] A. Gianfagna, R. Oberti, *American Mineralogist*, 86, 1489-93 (2001)
- [2] A. Gianfagna, P. Ballirano, F. Bellatreccia, B. Bruni, L. Paoletti, R. Oberti, *Mineral. Magazine*, 67, 1221-9 (2003)
- [3] P. Comba, A. Gianfagna, L. Paoletti, *Arch. Environm. Health*, 58, 229-32 (2003)
- [4] A. Gianfagna, L. Paoletti, P. Ventura, *PLINIUS, suppl. EJM*, 18, 117-9 (1997)
- [5] L. Paoletti, D. Batisti, C. Bruno, M. Di Paola, A. Gianfagna, et al., *Arch. Environm. Health*, 55, 392-8 (2000)
- [6] V. Cardile, M. Renis, C. Scifo, L. Lombardo, R. Gulino, et al., *Intern. J. Bioch. Cell Biol.*, 36, 849-60 (2004)
- [7] M. Soffritti, F. Minardi, L. Bua, D. Degli Esposti, F. Belpoggi, *Eur. J. Oncol.*, 9, 169-75 (2004)
- [8] A. Gianfagna, S. Mazziotti-Tagliani, A. Pacella, L., *GEOITALIA, Spoleto, Vol. Abstracts*, (2005)
- [9] C. Rinaudo, D. Gastaldi, S. Cairo, A. Gianfagna, et al., *GEOITALIA, Spoleto, Vol. Abstracts*, (2005)
- [10] B.E. Leake, A.R. Woolley, C.E.S. Arps, W.D. Birch, et al., *American Mineralogist*, 82, 1019-1037 (1997)
- [11] F. Burrigato, P. Comba, V. Baiocchi, D.M. Palladino, S. Simeì, et al., *Environm. Geology*, 47, 855-68 (2005)

ASBESTOS CONTAINING MATERIAL MAPPING OF EMILIA-ROMAGNA REGION: APPLICATION OF 18 D.M. 101/2003

E. Renna, F. Paoli, O. Sala, G. Pecchini, T. Bacci, V. Biancolini

ARPA Emilia-Romagna sez. provinciale di Reggio Emilia

Law D.M. 101/2003 previews asbestos containing material (acm) mapping realization; Emilia-Romagna Region has entrusted to ARPA this task with the specific purpose to map:

1. industries with friable or compact asbestos materials;
2. industries not in use;
3. public buildings with presence of compact or friable asbestos (school, hospitals, , sport areas, supermarkets, penitentiaries, cinema, theatres, libraries and church);
4. Areas with natural asbestos presence - *greens stone*;

The conference of the Councillorships to the Health and the Environment and the Conference of the Regions' s Presidents have indicated the algorithm (with twenty indicators) to determine the urgent asbestos decontaminations. ARPA also has characterized the parameters that mainly contribute to the allocation of the scores.

Network ARPA (Servizi Territoriali, Servizi Sistemi Ambientali and in particular Eccellenza Amianto of Reggio Emilia that has coordinated the job) has contacted more than 4000 public and private structures and has executed more than 1300 inspections.

Every site has been geocoded through standards SINANET like from DM 101/2003; the collected data have been organized in a geographic informative system (GIS) that concurs both the cartographic visualization to various levels of detail (regional, provincial, communal, for category, priority and score) and the consultation of the data and the report reassumed associates to every site.

The regional data have been subdivided in the three groups:

1. "productive activities" understandings as industries in use and not;
2. "sensitive and scholastic population" understandings like schools and hospitals;
3. "free time" meant like libraries, churches, supermarkets, sport areas, cinema and theatres.

Results:

- Altogether the scores turn out lower of the maximum obtainable score (6268) to demonstration of the insignificance of serious situations (Table 1);

Tab.1 Bands of score

< 500	500÷1000	501÷1500	1501÷2000	≥ 2000
27%	31%	40%	1.6%	0.4%

- The acm has been found mostly in compact matrix, above all like cover in concrete-asbestos (Table 2);

Tab.2 - Asbestos containing material

Roof	Paving	Other
70%	13%	17%

- More than 60% cases have a good state of conservation, the damages are smaller than 10% (Table 3);

Tab.3 state of conservation of the acm

damages < 10%	damages ≥ 10%	not indicated
10%	10%	
65%	27%	8%

- The situations with friable asbestos presence are limited thanks to the numerous asbestos decontamination realized from the census of 1997 of the Emilia-Romagna Region (Table 4);

Tab.4 – Typology of amc

compact	friable
90%	10%

- the productive activities have great extension connected to their constructive typology and their use (Table 5);

Tab.5 – Extension of site

	<500 mq	500÷5000 mq	>5000 mq	not indicated
productive activities	10%	16%	74%	1%
public buildings	10%	53%	36%	1%

- the public buildings are found mostly to the inside of urban centers where the population density is greater; part of the productive activities (50%) is placed outside from the urban centers and remaining 50% (Tables 6 and 7).

Tab. 6 – Distance from the live center

	beyond 1000 m	within 1000 m	urban center	not indicated
productive activities	50%	22%	28%	0%
public buildings	4%	11%	84%	1%

Tab. 7 – Density of interested population

	scattered houses	built-up area	not indicated
productive activities	60%	38%	2%
public buildings	13%	86%	1%

BIBLIOGRAFY

1. D.M. 101 del 18 marzo 2003 (regolamento attuativo della L. 93 del 23 marzo 2001)
2. Conferenza delle Regioni: Procedure per la determinazione delle priorità di intervento (2004)

ENVIRONMENTAL POLLUTION FROM AIRBORNE ASBESTIFORM FIBRES: DEVELOPMENT OF FIBRE PROPAGATION MAPS

F. Burragato¹, M. Crispino², A. & F.³ Monti, L. Papacchini³, F. Rossini⁴, B. Schettino⁵, B. Sperduto⁶

1 - Dipartimento Scienze della Terra, Università "La Sapienza" Roma

2 - ARPA Regione Basilicata Potenza

3 - Ufficio Speciale Prevenzione e Protezione, Università "La Sapienza" Roma

4 - Dipartimento Produzione Vegetale, Università della Tuscia Viterbo

5 - ASL Lagonegro (Basilicata)

6 - Centro Igiene Industriale, Università Cattolica del Sacro Cuore Roma

Environmental pollution from airborne asbestos fibres (and asbestos-related deaths from malignant pleural mesothelioma) poses a challenge in terms of risk exposure assessment. Use is generally made of GIS methodologies, such as fibre propagation maps. These maps rely on parameters that are in part measured and in part estimated and then processed with map-algebra operations.

Fibre propagation maps may be built on the basis of geolithological features, land use, distance from the source, dominant weather conditions, etc. Conversely, fibre inhalation risk assessment requires careful and accurate sampling surveys and analyses.

The location of sampling stations (adequately equipped for monitoring weather conditions and climate) may be easily identified by resorting to a geographic map of the fibre dispersion risk¹. Airborne fibre concentrations are instead determined via Phase Contrast Light Microscopy (PCLM) with an analytical procedure designed for workplaces (D.Lgs. 277/91) and thus unsuitable for non-occupational asbestos exposure measurements. If analytical sensitivity were higher, estimated parameters might be replaced by measured parameters, thus making fibre propagation maps more reliable.

Using the current analytical procedure and the Walton-Beckett eyepiece graticule and exploring 100 fields per 1,000 litres of sampled air, as little as 0.23% of the filter surface is examined, with a detection limit of 0.22 f/l. This is tantamount to saying that there are 221 fibres on the filter, i.e. 221 f/m³. If the number of explored fields were increased to 400, less than 1% of the sampling filter surface would be explored, which would not significantly improve the sensitivity of the procedure. Mortality rates in non-occupational settings suggest that even few fibres per cubic metre are an indicator of real risk, especially if tremolite fibres are involved^{2,3}.

Extending filter exploration to full field (excluding the Walton-Beckett graticule) increases the examined filter surface 25 times and decreases the detection limit 25 times, explored fields remaining equal.

For counting 200 fields, the detection limit is 0.004 f/l with full-field examination, as against 0.11 f/l with the WB graticule examination, corresponding to 4 f/m³ and to 110 f/m³, respectively (see Table).

Total Detected Fibres	No. of Explored Fields	Litres of Sampled Air	Concentration f/l		Fibres on Filter		% of Explored Filter	
			Full field	WB	Full field	WB	Full field	WB
1	100	1000	0.018	0.44	18	441	5.67	0.23
1	200	1000	0.009	0.22	9	221	11.34	0.45
0.5	100	1000	0.009	0.22	9	221	5.67	0.23
0.5	200	1000	0.004	0.11	4	110	11.34	0.45
0.5	400	1000	-	0.06	-	55	-	0.91

As is obvious, if the number of fibres on the filter decreases, the error in estimating their concentration tends to increase and increasing the explored surface area may not offset such error. With this consideration in mind, counting of fibres on the filter was simulated by using a very straightforward algorithm:

- 1) 200 disks of radius R were evenly distributed on a circle of radius 11;
- 2) N points (fibres) were randomly and uniformly distributed on the circle;
- 3) when R was increased from 0.025 to 0.250, the number of fibres falling within the disks of radius R was counted.

The number of fibres on the filter was changed from a maximum of 300 to a minimum of 10. In all cases and as expected, the estimated concentration was significantly error-affected and increasing the explored surface area failed to promptly correct the error. However, the ratio of fibre counts to the explored surface area remained practically constant (Fig. 1).

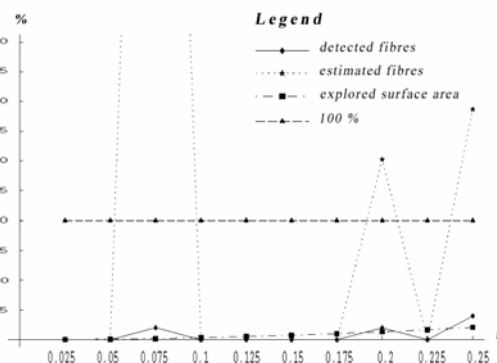


FIGURE 1: percentages of detected fibres and explored surface area when increasing radius r for a filter with 10 fibres

By contrast, when use was made of the average of the estimated values (obtained on n filters with the same total number of fibres) rather than of the results of the individual filters, then the increase of the explored surface considerably reduced estimation uncertainty.

Fig. 2 shows the average of estimated values for only 5 filters, each with a total of 10 fibres.

In actual fact, the average is taken on a much higher number of samples. Therefore, this result appeared as particularly encouraging.

With a view to determining the minimum number of samples required for a fairly reliable estimation of the average, the variance change with the explored area was investigated.

Now, if the random variable representing the result of the experiment (estimation of number of fibres on a filter) is denoted with X and its (a priori known) expected value with μ , then repeating the test with n filters yields independent and identically distributed random variables X_i . Hence, the expected value of the random variable

$Y = \frac{1}{n} \sum_{i=1}^n (X_i - \mu)^2$ with a sufficiently high n will be the variance of X .

Computing the variance upon the change of the explored surface area for $n=100$ and $n=500$ gives a value which is proportional to the inverse of the explored surface area, as shown in Fig. 3 (100 filters, each with a total of 10 fibres). In other words, variance decreases with the square of the field radius. This finding is very encouraging, because it confirms that: i) increasing the diameter of the observation field 5 times (full-field observation) improves the detection limit 25 times; and ii) this analytical procedure also provides the most reliable results.

Finally, Fig. 4 displays the results of analyses conducted on 17 filters. The air samples were collected from a site with tremolite fibre-bearing serpentinite outcrops. PCLM analyses were carried out on 200 fields, counting the fibres in the full field and in the WB graticule. The difference between the two procedures is clear. All the results obtained with the WB graticule are overestimated or null, thus unreliable for estimating an average value; conversely, full-field analyses give much more homogeneous results with only two null values and can be easily averaged.

These preliminary experiments are far from conclusive; therefore, more in-depth theoretical and experimental investigations are needed.

References

- Burrigato F., Mastacchi R., Papacchini L., Rossini F., Sperduto B. (2004) Mapping of risk due to particulates of natural origin containing fibrous tremolite: the case of Selci di Lauria (Basilicata, Italy). Modelling, computer assisted simulation and mapping of natural phenomena for hazard assessment – Geophysical Research Abstracts Volume 6, 2004
- Luce D, Bugel I, Goldberg P, Goldberg M, Salomon C, Billon-Galland MA, Nicolau J, Quénel P, Fevotte J, Brochard P (2000) Environmental exposure to tremolite and respiratory cancer in New Caledonia: a case-control study. *Am J Epidemiol* 151:259-265
- Hillerdal G (1999) Mesothelioma: cases associated with non-occupational and low dose exposure. *Occup Environ Med* 56:505-513

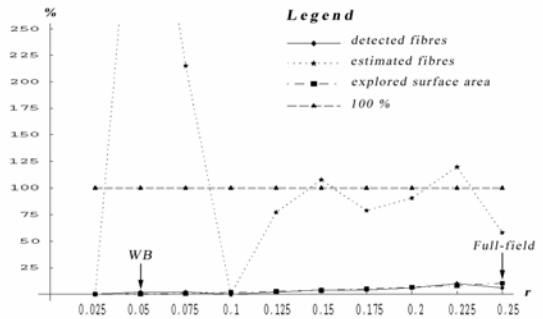


FIGURE 2: averages of percentages of detected fibres and explored surface area on 5 filters (each with 10 fibres) when increasing radius r

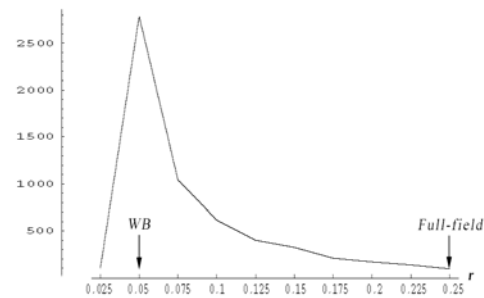


FIGURE 3: variance upon the change of r for $n = 100$

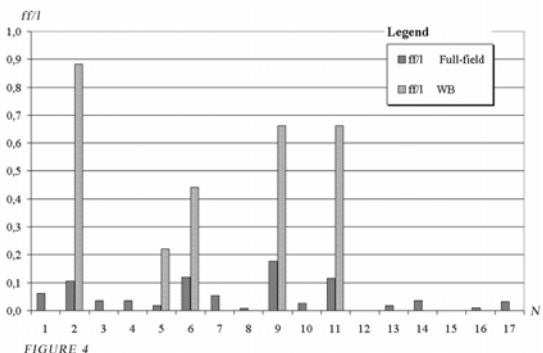


FIGURE 4

MAPPING OF THE ASBESTOS-CEMENT BY REMOTE SENSING AND GIS

L. Fiumi, C. Atturo, G. Fontinovo

CNR Institute for the Atmospheric Pollution – LARA (Laboratorio Aereo Ricerche Ambientali - Airborne Laboratory for Environmental Research), Roma Italy

At present, monitoring of asbestos-cement roofing is essentially based on direct detection, normally carried out by experts from the Local Health Authority (ASL)]. According to this approach, the detection of contaminated sites however causes a series of logistical difficulties with subsequent economic repercussions, above all when the investigation involves extensive territorial surfaces. An interesting alternative to traditional detection is aero-space remote sensing. It is not always possible however to obtain detailed analyses such as the exact identification of asbestos-cement roofing using satellite remote sensing technology because of resolution limits. The high potential of the multispectral investigation with MIVIS data (102 investigative bands) with refined radiometric discrimination (pushed up to 0.02 microns) of the sensor itself, used with the conventional characteristics of remote sensing data, makes a very interesting instrument, allowing an analysis never before carried out on an operative level.

The MIVIS images used for this study were taken above Rome on 20 June 1995 at 12:30 according to a N-S flight line at an altitude of 2000 m. A spatial resolution of 4m x 4m resulted. The study area examined corresponds to a subscene of 755 columns x 430 lines. The data analysis was carried out on a PC with digital image development software.

Not having reflectance measures to the ground and information on the characterisation of the column of air between the sensor and the ground at our disposal, the calibration method known as IARR (International Average Relative Reflectance). This consists in dividing the radiance of the spectrum of each pixel of the flight line by the average spectrum of the total view. This procedure is a variation of the so-called criterion known as "flat field calibration", which roughly removes solar irradiation, atmospheric absorption, scattering effects and every other residual noise from the instrument.

The data, radiometrically corrected, was classified using the Spectral Angle Mapper (SAM). The SAM allows a rapid mapping of the similarities of image spectrums with reference spectrums]. The reference spectra can be determined in laboratories or in the field or extracted from the image. The algorithm determines the spectral similarity between the two spectra through the calculus of the "angle" which they form, thus treating these as vectors in one space with the dimensionality equal to the number of bands.

The algorithm SAM, implemented through the commercial software ENVI], requires a number of trial areas (training areas) as input or reference spectrums deriving from specific Regions Of Interest (ROI) or banks of spectral data.

The input spectra were extracted from ROIs that were accurately identified in the view, through the visual analysis of colour stereo photo areas, on a scale of approximately 1:11 000 on 27 September 1988 (kindly provided by ENEL), integrated with a series of accurate observations of places and the visual analysis of additive syntheses in RGB (Red, Green, Blue).

In this phase of the method 13 ROIs corresponding to other materials were identified. A brief description follows.

Tiles and Bricks, Grit, Asbestos-cement, Cement surfaces, Metallic surfaces (sheets), Bituminous Surfaces, Pozzolan surfaces, Other surfaces, Roads, Treed surfaces, Bushed surfaces, Water

From the confusion matrix in this classification the results were as follows: the total classification accuracy obtained was equal to 84.6%; most of the classes were extracted with a variable accuracy of between 83% and 100%; similarly significant but not considerable is the classification accuracy of the only surfaces in asbestos-cement which in this first analysis is equal to 94.12%.

The study area was then detected by visual observations *in situ* with the aim of validating the results of MIVIS data classification. As well as the visual inspection of each building with asbestos-cement roofing, additional data and information were collected by means of forms filled in by owners and/or tenants. In addition, samples of material taken from roofs characterized as made of asbestos-cement were collected. These samples were afterwards analysed in a laboratory by means of different technique of microscopy, in collaboration with ISPESL, Dust and Fibres Laboratory.

From the results obtained through the aforementioned inspection, a fair number of areas was selected to test the classification accuracy which proved to be equal to 94.12%.

Based on the consideration that studies on urban-environmental problems should not neglect any elements at all, and a single GIS system can represent the best software environment for developing and experimenting this kind of investigations, since it enables the comprehensive and integrated use of data analysed (maps and remotely sensed data) and geo-coded, the research group made the choice of developing a specific system for the above described analysis.

GIS actually represents an important instrument for analysing territory and developing land management and planning models which can also involve a big number of sizes, associated to the graphic reference, with a high spatial variability.

In view of the multidisciplinary character of this work and the integration of data of different origin, the system created presents the following aims:

- Prediction aim (location and study and asbestos-cement roofing with the aim of assessing the connected risk).
- Comparison aim (acquisition of data and information about single buildings).
- Knowledge and training aim (choice of actions to be undertaken by ASLs).
- Statistical aim (data storage, data management and processing to define the land maintenance strategies of ASLs and other local Authorities).

The system was designed in order to be easily used also by inexperienced user with the task of inputting and managing data. It was planned and structured both for direct operations (data updating, inspection of abatement plans, etc.), and

post-processing operations. Based on data collected *in situ* this post-processing phase allows the evaluation of the distribution of asbestos in territory studied and the assessment of asbestos-related risk for workers and residents. The research group so opted for a simple, immediate and easily usable architecture.

The fundamental map is an abstract of the sheet 374 of the Technical Regional Chart of Lazio, at the scale 1:10 000, geo-coded by UTM-ED50 system. This map is integrated with an IKONOS satellite image in RGB in order to have an immediate visual reference.

In the first phase of realization of the GIS, data and information about the elements characterizing the study area, like Roads, Asbestos-Cement Roofing, Decontaminated Roofing, and ISTAT Data, were gathered.

Each element collected in the territory was geographically located and put into shapes, on the basis of which some relations were created in order to enable overlays and spatial analyses to be carried out.

The shapes implemented in this phase are simply territorial study elements present in the sample area.

Asbestos-cement roofing. Maps were produced by processing MIVIS data and validating them as previously mentioned. Decontaminated Roofing, according to the information received from ASLs about decontaminations already carry out and then inspected *in situ*.

Roads, present in the study area. The choice of viewing toponymy was suggested by ASLs to make the task of inspecting buildings easier.

ISTAT data. The study area was subdivided into sections according to the subdivision of 1991 census; residential density values were associated to each section.

In the second study phase the GIS architecture, organized on different informative levels, was integrated with data collected through accurate inspections *in situ* as above mentioned. These data include declarations made by owners/tenants in forms and Abatement Plans presented to ASLs. All this information was gathered into tables on the characteristics of roofing, and an informative database on roofing present in the study area was then created.



Figure1 – Shape of asbestos-cement roofing

The system proposed in this study, which is still being prepared as already mentioned, represents the first effort for defining a procedure able to map, assess, and more in general, to characterize asbestos-cement roofing present in urban areas, by using innovative instrument of investigation and spatial analysis such as GIS and remotely sensed data.

As aforesaid, the integration of these two techniques of environmental monitoring enables an unlimited number of heterogeneous variables, which can be integrated and interrelated each another, to be rapidly managed.

The work carried out so far for defining criteria and methods is addressed not only to researchers but also and above all to public Authorities which have always to face so many difficulties in assessing with precision and reliability information about territory under their jurisdiction, and which can so take benefit from this sort of studies.

References

- Boardman J.W., Kruse F.A. (1994), "Automated spectral analysis: a geological example using AVIRIS data, North Grapevine Mountains, Nevada", Proceedings of Tenth Thematic Conference on Geologic Remote Sensing, San Antonio Texas USA, Vol. I, 407-418.
- D.M. della Sanità 6 settembre 1994, "Normative e metodologie tecniche di applicazione dell'art. 6, comma 3, e dell'art. 12, comma 2, della legge 27 marzo 1992, n. 257, relativa alla cessazione dell'impiego dell'amianto". Supplemento Ordinario alla Gazzetta Ufficiale, Serie generale, n. 288, del 10/12/1994.
- D.M. dell'Ambiente e della Tutela del Territorio 18 marzo 2003, n.101, "Regolamento per la realizzazione di una mappatura delle zone del territorio nazionale interessate dalla presenza di amianto, ai sensi dell'articolo 20 della legge 23 marzo 2001, n. 93". Gazzetta Ufficiale del 09/05/03.
- Fiumi L., Campopiano A., Casciardi S., Fioravanti F., Ramires D. (2000), "Mappatura e valutazioni dello stato delle superfici in cemento-amianto attraverso telerilevamento aereo", Atti del Symposia I Congressi della fondazione Maugeri, Vol.4, 2000 Pavia, 175-177.
- Palumbo A. (2001), "Metodologie per la valutazione dell'inquinamento di un acquifero mediante tecniche GIS", Documenti del Territorio Anno XIV, N. 47/2001, pp.52-54.

Session: Indirect biological methods

- S. Capella Indirect monitoring of asbestos by mineralogical investigations of sentinel animals lungs
- M. Tomatis Asbestos fibres in human urine reflecting environmental exposure measured by long and short term air monitoring in the lanzo and susa valleys
- T. Battaglia Monitoring of respirable mineral fibres in the biancavilla area (sicily) by sem-eds analysis of urine
- E. Fornero A cattle model of environmental exposure to asbestos in lanzo and susa valleys (piedmont region): possible fibre accumulation mechanism in cow lungs
- D. Bellis Mineralogical investigation of human biological material to detect the presence of breathable mineral fibres in airborne dust

INDIRECT MONITORING OF ASBESTOS BY MINERALOGICAL INVESTIGATIONS OF SENTINEL ANIMALS LUNGS

S. Capella^{1,3}, E. Fornero^{1,3}, E. Belluso^{1,3,4}, D. Bellis^{2,3}, G. Ferraris^{1,3,4}, F. Carlone², B. Bruni⁵, L. Paoletti⁵

¹ Dipartimento di Scienze Mineralogiche e Petrologiche – Università degli Studi di Torino

² Servizio di Anatomia, Istologia Patologica e Citodiagnostica – ASL4 – Torino Nord Emergenza San Giovanni Bosco

³ Centro Interdipartimentale per lo Studio degli Amianti e di altri Particolati Nocivi “G. Scansetti” - Università degli Studi di Torino

⁴ CNR IGG – Sezione di Torino

⁵ Istituto Superiore di Sanità - Roma

Recent publications show the advantage in using animal populations (named animal sentinel systems) as indicator of airborne pollutants (e.g., asbestos). The animals are not subject to professional exposure and their tissues are easier to obtain than the human ones. For these reasons, it seems a good choice investigate animal tissues, when appropriate. The results obtained from the investigation of 24 lung samples (18 from cows; 6 from wild animals) are here presented.

The selected samples are representative of different geological areas of the Piedmont Region (North-Western Italy): the Lanzo Valley and the Varaita Valley are areas with outcropping rocks bearing tremolite and chrysotile asbestos (serpentinites); the Asti area is geologically free of asbestos and has been chosen as control case.

For this investigation we use a protocol standardized by us. It is based on:

- a) sampling and preparation of lung tissues
- b) counting of asbestos bodies by optical microscopy;
- c) identification and quantification of mineral fibres by SEM-EDS and eventually by TEM-EDS;
- d) comparison between the obtained mineralogical data with the minerals identified in airborne dust from the living area of the studied animals and those occurring in the rocks of the same area.

Fifteen different mineralogical fibrous species have been identified in the observed samples. In the Asti area, control case (group I) both the number and the variety of fibres is lower than in the lungs of animals that lived in alpine areas close to outcrops of serpentinite (group II). In particular, the presence of chrysotile and tremolite asbestos in lungs of group II animals is clearly correlated with the mineralogical content of outcropped rocks in the Lanzo and Varaita valleys. The comparison between (a) the significantly high number of animals of the Asti group for which no fibres have been detected, and (b) the constant occurrence of fibres in the samples from the test alpine animals, leads to the following conclusion: the proposed method definitely can discriminate between the lower lung burden expected for a population living in an environmental-safe area (Asti) and the higher lung burden expected for a population living in an environmental risk-area where fibre-bearing rocks occur (Western Alps).

Our results show that the proposed technique is useful to determine type and quantity of inorganic fibres that occur as background in the natural environment and confirms the advantage of using lungs animals, instead than human tissues, to monitor the background level of breathable inorganic fibres in natural environment.

ASBESTOS FIBRES IN HUMAN URINE REFLECTS ENVIRONMENTAL EXPOSURE MEASURED BY LONG AND SHORT TERM AIR MONITORING IN THE LANZO AND SUSAL VALLEYS (PIEDMONT REGION).

M. Tomatis^{1,4}, E. Fornero^{2,4}, C. Groppo^{2,4}, F. Turci^{1,4}, D. Bellis^{3,4}, L. Bruna⁵, P. Piazzano⁵, G. Schellino⁵, B. Fubini^{1,4}, E. Belluso^{2,4,6}

¹ Dept. of Chemistry IFM, University of Torino, Italy

² Dept. of Mineralogical and Petrological Sciences, University of Torino, Italy

³ Servizio di Anatomia, Istologia Patologica e Citodiagnostica – ASL4 – Torino Nord Emergenza San Giovanni Bosco, Italy

⁴ Interdepartmental Center “G. Scansetti” for Studies on Asbestos and other Toxic Particulates, University of Torino, Italy

⁵ Assessorato all'Ambiente, Regione Piemonte, Italy

⁶ CNR-IGG Torino, Italy

In some areas of the Piedmont Region (North Western Italy) rich in serpentinite rocks, asbestos fibres may become airborne. The evaluation of the environmental background and of the respirable portion could improve the knowledge on possible hazard low dose exposure to asbestos.

In the context of a multidisciplinary research on asbestos risk in two Piedmont valleys – Lanzo Valleys and Susa Valley – we have carried out sampling of airborne particles and human urine. The presence of particulate matter in the urine may

be the result of the penetration through the lung or through the gastrointestinal tract, respectively, of inhaled or ingested particles.

The airborne samples were collected in areas close to serpentinite rocks, without anthropic activities, both for short (few hours, using a portable sampler for personal air monitoring) and long (one month, using a sampling device for atmospheric depositions) periods of times.

The urine samples were collected from volunteers without asbestos occupational exposure. These biological samples were prepared by chemical digestion in sodium hypochlorite and filtering.

The filters obtained both from air sampling and from urine have been examined by SEM-EDS in order to identify and quantify asbestos fibres.

Several remarks are possible:

airborne samples

- in both valleys the average concentration of total airborne fibres, both asbestos and not asbestos, was similar (1,6 fibres/L and 1,3 fibres/L for the Susa and Lanzo valleys respectively)
- asbestos fibres were always found in a low concentration (0,2 and 0,3 fibres/L respectively for Susa and Lanzo Valleys)
- the chrysotile-antigorite group was the most frequent and abundant in both valleys, tremolite fibres were found in about half of the airborne samples collected, whereas actinolite was only occasionally found.

biological samples

- the 66% of urine samples contained mineral fibres (asbestos or non asbestos): the asbestos fibres were found only in a few percentage of samples analysed
- the chrysotile-antigorite group was the most frequent in the urine of both valley similarly to the airborne samples, but tremolite fibres were found only in the urine from Susa Valley

The present data (presence of mineral fibres in the urine, some analogy between the mineral content of biological and airborne samples) might suggest such biological samples could be used as indicator of environmental exposure.

MONITORING OF RESPIRABLE MINERAL FIBRES IN THE BIANCAVILLA AREA (SICILY) BY SEM-EDS ANALYSIS OF URINE

T. Battaglia¹, E. Belluso^{2,6,7}, S. Capella^{2,6}, E. Fornero^{2,6}, G. Ferraris^{2,6,7}, D. Bellis^{3,6}, G. Biagini⁴, A. Pugnaloni⁴, A.M. Panico⁵, V. Cardile⁵

¹ Dipartimento di Scienze Farmaceutiche - Università degli Studi di Catania

² Dipartimento di Scienze Mineralogiche e Petrologiche – Università degli Studi di Torino

³ Servizio di Anatomia, Istologia Patologica e Citodiagnostica – ASL4 – Torino Nord Emergenza San Giovanni Bosco

⁴ Istituto di Morfologia umana normale – Università Politecnica delle Marche, Ancona

⁵ Dipartimento di Scienze Fisiologiche - Università degli Studi di Catania

⁶ Centro Interdipartimentale per lo Studio degli Amianti e di altri Particolati Nocivi "G. Scansetti" - Università degli Studi di Torino

⁷ CNR IGG – Sezione di Torino

Optical Microscopy (OM) is the method currently used to assess asbestos exposure via the search for Asbestos Bodies (ABs) in bronchoalveolar lavage (BAL) and in (autopic/biopic) human tissues. This technique however is not suitable to give information neither on the fibre species nor on the time exposure.

The presence of mineral fibres in urine [1] is considered an indicator of recent exposure at a temporal scale from days to few months. The urine, in fact, as final product of kidney filtration, not only can give information on respired/ingested fibres burden, but even on the clearance mechanism. We examined mineral fibres in urine samples by SEM-EDS, using a technique standardised in our laboratory; it is not invasive and can represent a complementary/alternative method.

We monitored the environmental exposure to fibres of the amphibole fluoro-edenite in the Biancavilla area (Catania – Sicily Region). This kind of fibres, in fact, are abundant in autochthon lava rocks that were locally used as building material until few years ago and their presence has been correlated with an excess of malignant mesothelioma (neoplasia related to asbestos occupational exposure). For this research, urine of 15 people living in Biancavilla and not professionally exposed have been examined (Group I). The samples have been collected in September 2004. The results obtained from the Biancavilla samples have been compared with those of a control population, represented by 20 people living in Asti, Piedmont Region (Group II).

14 fibrous inorganic species have been detected in the urine of 13 samples out of 15 belonging to Group I: 7 phyllosilicates; 3 inosilicates; 1 vitreous fibre containing Al and Si, silica, feldspars, metal oxides/hydroxides. The phyllosilicates correspond to species contained in building materials and account for 10 % of the total number of fibres. Among the observed fibres of inosilicates, the calcic amphiboles (tremolite and edenite) are more abundant (3.6 %) than pyroxenes (enstatite: 1.6%). Silica, feldspars, metal oxides/hydroxides represent 4.8%. The vitreous fibres account for 80 % of the observed fibres. Its high quantity is likely to be ascribed to an abundant and widespread presence in many industrial products. The presence in urine of the mentioned silicates has to be considered as correlated to environmental exposure to airborne particulate because the ingested portion can be considered negligible [1]. Taking into account the biological scale of time, the fibres detected in the urine samples have been respired during summer 2004 (Spring at most).

Fibrous inorganic species have been detected only in the urine of 1 out of 20 samples belonging to Group II (control): 2 phyllosilicates and 2 inosilicates; the other 19 samples were fibre-free. Our results confirm that fibres are able to migrate, via blood, through the organism and reach urine. They show also that it is possible to obtain information on the exposure type, discriminating between environmental and occupational exposure.

References

- [1] Cook P M, Olson G F, *Science*, 204, 195-198 (1979)

A CATTLE MODEL OF ENVIRONMENTAL EXPOSURE TO ASBESTOS IN LANZO AND SUSA VALLEYS (PIEDMONT REGION): POSSIBLE FIBRE ACCUMULATION MECHANISM IN COW LUNGS

E. Fornero^{1,4}, D. Bellis^{2,4}, M. Tomatis^{3,4}, L. Bruna⁵, P. Piazzano⁵, G. Schellino⁵, E. Belluso^{1,4,6}, B. Fubini^{3,4}

¹ Dept. of Mineralogical and Petrological Sciences, University of Torino, Italy

² Servizio di Anatomia, Istologia Patologica e Citodiagnostica – ASL4 – Torino Nord Emergenza San Giovanni Bosco, Italy

³ Dept. of Chemistry IFM, University of Torino, Italy

⁴ Interdepartmental Center "G. Scansetti" for Studies on Asbestos and other Toxic Particulates, University of Torino, Italy

⁵ Assessorato all'Ambiente, Regione Piemonte, Italy

⁶ CNR-IGG Torino, Italy

Outcrops of serpentinite rocks, bearing tremolite and chrysotile asbestos, largely occur in the Italian Western Alps (Susa and Lanzo valleys- Internal Piemonte Zone). In order to evaluate environmental exposure to airborne fibres, the mineralogical burden of cattle lungs has been investigated. Each sample of lung was digested in a hypochlorite solution, then filtered and examined by microscopic techniques. The investigation has been carried out on about forty cows by MO and by SEM-EDS in order to detect ferruginous bodies (fb) and to identify and quantify the mineralogical fibrous species respectively. Cows appear to be a good tool for monitoring environmental exposure to particles.

The data obtained, reported below, indicate that:

- a) as expected for non-occupational exposure, the fb in animals are very uncommon. When detected they are in a small quantity, less than 183 fb/g_{dw} (for professional exposure the cut-off internationally adopted is 1000 fb/ g_{dw})
- b) the concentration of total inorganic fibres found in both valleys is comparable (about 100.000 ff/ g_{dw}) and the amount of asbestos fibres in the lungs was similar too. In the Susa valley cattles, five asbestos species, which are listed in order of decreasing frequency, are found: tremolite, actinolite, amosite, crocidolite, chrysotile. In the Lanzo valley cattles, four asbestos species are found (in the same order listed above): tremolite, actinolite, amosite, and chrysotile. The first two are asbestos occurring in the natural environment, in fact they are present in very abundant and outcropping serpentinite rocks in the areas investigated, but they have not been industrially used. Amosite and crocidolite are asbestos related strictly to anthropogenic products because they are not present in rocks in these areas as in all the Italian country. Chrysotile could originate from both natural and anthropogenic source being both industrially used and frequent in the rocks of these valleys. By the used technique, only in a very few cases chrysotile can be distinguished from fibrous antigorite (an other mineral of serpentine group) and therefore in other cases we have indicated them are chrysotile-antigorite. The natural asbestos tremolite is the most frequent asbestos found in both valleys and in similar concentration. Also the chrysotile-antigorite group is abundant and frequent, but his concentration in Lanzo valleys is almost six time more than in Susa valley
- c) when the amount of asbestos fibres has been related with the age of the animals, although the number of samples is not yet statistically significant, a correlation is found between the concentration of asbestos fibre and the age/time of exposure, for heavy exposure (when a threshold of about 33.000 ff/g_{dw} is overcome), where clearance is probably impaired. For lower exposure, when clearance equilibrates deposition, no age effect is detectable, as expected.

MINERALOGICAL INVESTIGATION OF HUMAN BIOLOGICAL MATERIAL TO DETECT THE PRESENCE OF BREATHABLE MINERAL FIBRES IN AIRBORNE DUST.

D. Bellis^{1,3}, E. Belluso^{2,3,4}, S. Capella^{2,3}, E. Fornero^{2,3}, S. Coverlizza¹, G. Ferraris^{2,3,4}

¹ Servizio di Anatomia, Istologia Patologica e Citodiagnostica – ASL4 – Torino Nord Emergenza San Giovanni Bosco

² Dipartimento di Scienze Mineralogiche e Petrologiche – Università degli Studi di Torino

³ Centro Interdipartimentale per lo Studio degli Amianti e di altri Particolati Nocivi “G. Scansetti” - Università degli Studi di Torino

⁴ CNR IGG – Sezione di Torino

In the last years the number of legal actions related to the determination of relationships between professional exposure to asbestos and neoplasia is steadily increasing. At the same time, there is an increasing awareness of possible health hazards not related to professional exposure to asbestos and/or other mineral fibres, but related instead to the background of such fibres generated both by natural and anthropic events. Therefore, it is important to investigate biological samples (tissues and fluids) in order to: *i)* establish which inorganic fibrous dusts of the environmental background are breathable and persistent in the organism; *ii)* determine the environmental exposure to harmful inorganic fibres and to get epidemiological data. Literature data show that for biological samples, a standard approach to the sample preparation and examination and to the identification and quantification of particles does not exist. In this work, we propose a standard procedure based on SEM-EDS use to investigate the burden of mineral fibres in human biological samples.

Shortly, the steps of our procedure are:

- sampling of 0.5 g for tissues or 10 cc for fluids;
- chemical digestion of the biological material by sodium hypochlorite;
- filtering of the suspension through a membrane;
- washing of the membrane with warm distilled water;
- dehydration of the filter;
- clarification by acetone method to glue the membrane to the SEM aluminium pin stub;
- coating of the membrane with carbon to made the sample conductive;
- identification of inorganic fibrous by SEM-EDS and, for doubtful cases, by TEM-EDS;
- quantification of every fibrous species burden and standardisation to the number of fibres per gram of dry weight lung tissue.

According to our experience, the proposed protocol is rather efficient and potentially alternative to the TEM-EDS methods for the analyses of particles incorporated in biological materials, both fluid (as urine and bronchoalveolar lavage fluid; may be for blood - the test for this material is in progress) and solid (as lung, bladder, kidney, heart, liver, placenta). The solid materials can be fresh, fixed in formalin or included in paraffin.

In particular, the data we obtain show that the mineralogical investigation of human samples reveals not only the burden of fibres, but also their chemical and mineralogical nature. Thus, it is possible to obtain information on the type of environment and of exposure which provided the detected fibres, an aspect of paramount importance in case of legal actions and medical-epidemiological investigations.

Poster session

- | | |
|---------------|---|
| P. Avino | Fibrous material characterization in an urban area at high density of autovehicular traffic |
| A. Baj | Control of airborne fibres by scanning electron microscopy (SEM) and phase-contrast microscopy (MOCF) during asbestos removal |
| L. Bologna | Problems concerned with the natural presence of asbestos |
| V. Cardile | Involvement of oxidative stress and cyclooxygenase in the effects induced by the asbestos-like fluoro-edenite fibres |
| P. Di Pietro | Determination of asbestos in vinyl floor tiles by FT-IR technique |
| C. Fanizza | Polycrystalline fibre size distribution by SEM |
| L. Groppo | Quantitative analysis of chrysotile in antigorite-serpentinites using spectroscopic and thermal analysis |
| A. Gualtieri | Long-term asbestos monitoring in life and professional environments of selected Italian sites |
| P. Marescotti | Naturally occurring asbestos minerals from metaophiolites: rationales for custom-designed analytical constraints |
| S. Massera | Asbestos substitutive materials: analytical protocols for classification of man-made vitreous fibres as carcinogenic agents |
| G. Pecchini | Analytical evaluation of wastes containing asbestos after inertization treatment by pyrolytic process |
| S. Peterle | Airborne fibres in environments with vinyl-asbestos floors: risk assessment and prevention criteria |
| S. Prandi | Health environmental analysis of materials used for a beach nourishment in the Liguria coast |
| O. Sala | The Ophiolites: their extraction and the asbestos problem |
| A. Verardo | Training and information: consciousness and communication on the asbestos topic |

FIBROUS MATERIAL CHARACTERIZATION IN AN URBAN AREA AT HIGH DENSITY OF AUTOVEHICULAR TRAFFIC

P. Avino¹, P. De Simone², C. Fanizza², M. Manigrasso¹

¹Dipartimento Inseguimenti Produttivi ed Interazione con l'Ambiente, Laboratorio Chimico dell'Aria, Istituto Superiore per la Prevenzione E la Sicurezza del Lavoro, via Urbana 167, 00184 Rome, Italy

²Dipartimento Igiene del Lavoro, Laboratorio Polveri e Fibre, Istituto Superiore per la Prevenzione E la Sicurezza del Lavoro, via Fontana Candida 1, 00040 Monte Porzio Catone (Rome), Italy

The characterization of atmospheric particulate matter and fibrous material represents a very important aspect for the air quality evaluation and for their relative effects on the population both in industrial areas and a megacity.

The particulate, also called "aerosol" or "dust", is constituted by all the suspended non-gaseous material present in atmosphere. From the dimensional point of view the definition of the various kind of particulate contemplates four categories, according to the dimension of the particle aerodynamic diameter (d_a): ultrafine ($d_a \leq 0.1 \mu\text{m}$); fine ($0.1 \mu\text{m} \leq d_a \leq 2.5 \mu\text{m}$); coarse ($2.5 \mu\text{m} \leq d_a \leq 10 \mu\text{m}$); total suspended particulate. The chemical particle composition (carbonaceous fraction, organic fraction, metals, etc.) results important for the sanitary-toxicological aspect [1].

As regards the fibrous material in urban areas great part of the studies concerning the exposure of the general population have been based mainly on asbestos, while only a limited number of studies on nonoccupational exposures to mineral fibers have been published.

Considering the sanitary importance that the possible concomitant exposure of the population to fibrous material and particulate matter can involve, we performed a study finalized to the determination of the simultaneous presence of these pollutants in the urban area of Rome. To this purpose, the levels of organic carbon (OC), elemental carbon (EC) and PM₁₀ with their relative relationships and the evidence of presence of mineral fibers are here reported and discussed.

The measurement campaign was performed for 24-hours long during November-December 2003 at the ISPESL's Pilot Station in downtown Rome, near the Termini railway station.

Both for sampling and determination of numerical concentration of inorganic fibrous particles was followed the ISO/FDIS 14966 regulation [2]. All the samples were analyzed by scanning electronic microscopy (LEO 440 S) equipped with an energy dispersive x-ray spectrometer (INCA Oxford Energy 400).

The ISO/FDIS 14966 regulation [2] provided fiber identification, according to the chemical composition and then by using energy dispersive x-ray analysis, into asbestos, calcium sulphate and other inorganic fibers. The organic fibers were not counted. This method is used to measure the numerical concentration of inorganic fibrous particles with widths smaller than $3 \mu\text{m}$ and lengths exceeding $5 \mu\text{m}$. Calcium sulphate fibers must be detected because a high concentration of these fibers can negatively bias the results for probable asbestos fibers, but these fibers are not included in the final result.

For each fiber found, the criteria, i.e. length/width $> 3 \mu\text{m}$, length $> 5 \mu\text{m}$ and width $> 3 \mu\text{m}$, were always checked. Each structure was identified from its morphology and chemical composition.

For the PM, OC and EC analysis two different analyzers were used: a TEOM (Rupprecht & Patashnik Co, Albany, NY, USA) for the PM determination and an analyzer mod. APCM5400 (R&P) for OC and EC [1]. Both of them were equipped with a $10 \mu\text{m}$ sampling head.

Figure 1 showed the fiber concentration square root divided in two clusters, one relative to daytime period and another relative to night. Since fiber counting is the measurements of randomly placed fibers which may be described by a Poisson distribution, a square root transformation of the fiber count data will results in approximately normally distributed data.

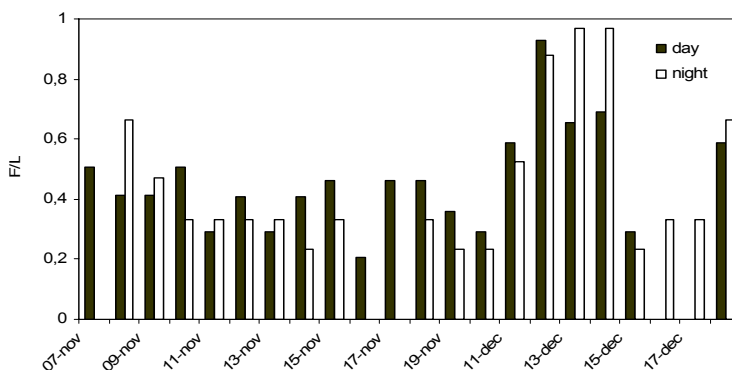


Figure 1 – Day/night fiber concentrations transformed for square root during the investigated periods.

Asbestos fibers were not found in any of the air sample. The only data reported in literature [3] determined in downtown Rome (Termini Station) in 1993 showed lowest asbestos fiber concentration values (0.1 Fiber/L), just 1-year later the application of the Regulation 257/92 [4].

MMVF fibers were detected in five days of measurement campaign, these fibers were identified both by elemental composition and by morphological criterion (lack of parallel edges). MMVFs found were of stone wool and glass wool. Numerous other inorganic fibers were detected, the combination of main components were Al, Mg, Si, Ca, Fe (even if they sometimes were not present simultaneously).

It was found that fibers containing calcium plus silicon and fibers containing only iron are the most frequent in the present study and they are also among the most frequent fibers present in urban area as reported by other authors [5,6]. The contribution of calcium sulphate fiber was negligible.

The difference fiber distribution between day and night showed in some days (Figure 1, 11th and 13th of November and 14, 17th-18th of December) are probably due to stability meteorological conditions present in those days.

In fact, Figure 2 shows the daily concentration trends of PM10 and total carbon (TC) determined in downtown Rome during December period. As it can be seen during the whole period there is a good relationship between the two pollutants: in particular, the correlation factor $R\ 0.883$ describes an high dependence of the PM10 from its carbonaceous fraction. This means a strict influence of anthropogenic sources in the particulate matter composition. In fact, considering the emission sources such as incomplete combustion and domestic heating, it is justified the high values of these two pollutants: PM10 reaches $180\ \mu\text{g}/\text{m}^3$ with an average value around $50\ \mu\text{g}/\text{m}^3$ while TC reaches $40\ \mu\text{g}/\text{m}^3$ with an average value around $15\ \mu\text{g}/\text{m}^3$.

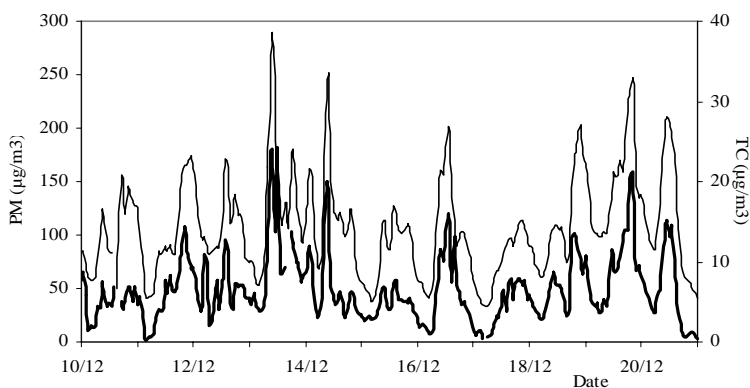


Figure 2 – Daily concentration trends ($\mu\text{g}/\text{m}^3$) of PM10 (bold) and TC (line) during December 10th-20th.

The data reported in this study are part of a project addressed to investigate the chemical composition of particulate matter (carbonaceous fraction and inorganic fibers) in relationship with the sanitary effects. In this way we have analyzed air samples collected in the same period inside a Roman green park (villa Ada) where the anthropogenic sources do not influence so much the air quality.

The preliminary results obtained in green area during the same period, i.e. November-December 2003, shows that the fibers containing silicon and calcium are the most abundant.

References

- [1] P. Avino, D. Brocco, L. Lepore, I. Ventrone, *J. Aerosol Sci.*, 31, S364-S365 (2000)
- [2] ISO 14966, *Ambient air - Determination of numerical concentration of inorganic fibrous particles - Scanning electron microscopy method*, 2002
- [3] G. Chiappino, A. Todaro, O. Blanchard, *Med. Lav.*, 84, 187-192 (1993)
- [4] Legge 27 marzo 1992, n. 257, *Norme relative alla cessazione dell'impiego dell'amianto*, 1992
- [5] D. Schneider, G. Burdett, L. Martignon, P. Brochard, M. Guillemin, U. Teicher, U. Draeger, *Scand. J. Work Environ. Health*, 22, 274-284 (1996)
- [6] J. Schnittger, in: *Faseförmige Stäube Verein Deutscher Ingenieure*. Verlag (Düsseldorf) 211-231, 1993

CONTROL OF AIRBORNE FIBRES BY SCANNING ELECTRON MICROSCOPY (SEM) AND PHASE-CONTRAST MICROSCOPY (MOCF) DURING ASBESTOS REMOVAL

L. Parrella¹, A. Bai², V. Gianelle³, F. Mandelli⁴

¹ Galileo Ambiente S.n.c., Milano, Italy

² Presidio Ospedaliero di Desio Unità Operativa di Medicina del Lavoro, Desio (MI), Italy

³ Agenzia Regionale Protezione Ambiente della Lombardia - Dipartimento di Milano, Milano, Italy

⁴ CM Cantieri Moderni S.r.l., Ranica (BG), Italy

INTRODUCTION

The operation of asbestos removal in some old factory plant was monitored using both SEM and MOCF in order to control the airborne fibres around the working area. The simultaneous monitoring by these two different techniques of analysis permitted an evaluation of the effectiveness of MOCF in ambient control during asbestos removal in abandoned industrial area.

Four asbestos removal sites were monitored, located in vary wide vacant industrial areas. Many technical difficulties rise from crumbling plants and buildings to reclaim. In particular it was often difficult to protect workers from risk of tottering structures and other risks for their safety.

In order to overcome these problems the asbestos removal was conducted with a new and original device (a little confined room placed over a travelling platform). The effectiveness of the confinement of working area was checked every day by ambient air sampling as requested by the local authority. The samples was analysed both with scanning electron microscopy (SEM) and phase-contrast microscopy (MOCF).

METHODS AND MATERIALS

Asbestos was removed from insulation of pipelines always located at a great height.

Number and size of pipes, height and kind of the location, state of preservation, was very different in the four sites monitored.

In one site, pipelines were insulated with friable material containing about 20% of amosite (amphibole form of asbestos), in the other three sites the insulation material was asbestos cement with about 10% of chrysotile.

The confined working room was a cab placed over a travelling platform, confined with polythene sheets. The air was pull out by an electrical aspirator with HEPA filters. The cab was risen near the pipes from which to remove asbestos and then polythene sheets were wrapped around the pipes to close the working room.

The airborne asbestos fibres were monitored inside the cab (working room) and outside it, both at the operative height and at ground level under the cab.

Ambient air was sampled with electrically powered pumps and membrane filters. In each point a sample for SEM analysis and a second sample for MOCF analysis were collected using the same sampling time but different flow rate (12 l/min for SEM and 3 l/min for MOCF) and different filter materials (polycarbonate for SEM and mixed cellulose esters for MOCF).

Altogether, 73 samples were collected and analysed by SEM and 73 other samples were collected and analysed by MOCF.

RESULTS AND CONCLUSIONS

Results obtained are statistically reported in the following table.

N° of samples	Sampling point	Airborne fibres (ff/l) S.E.M.		Airborne fibres (ff/l) M.O.C.F.		P t-test SEM vs MOCF
		average	Std. dev.	Average	std. dev.	
13	Inside the working room	463	88	548	712	0,63
12	Outside the working room. At the operating height on the left	2,9	4,7	3,4	4,3	0,28
11	Outside the working room. At the operating height on the right	1,1	0,9	2,4	1,4	0,02 *
20	Outside the working room. At ground level	1,8	3,5	1,6	1,2	0,82
16	Outside the working room. Near exhaust air manifold	1,3	1,6	2,1	2,0	0,01 *
8	Background pollution of the area without work in progress	0,4	0,1	0,4	0,3	0,91

* the difference between SEM and MOCF is statistically significant

The ratio between fibres concentration by MOCF and SEM was, on average, 1,76 (std. dev. 0,64).

Such results suggest a good agreement between the two analytical techniques (only two sampling points with a significant statistic difference).

Asbestos removal sites in vacant industrial areas are characterized of a modest presence of asbestos like fibres (i.e. cellulose fibres, textile fibres, etc.), so that MOCF is a useful mean to monitor airborne pollution and escape point of asbestos fibres from the confined working room.

Man made mineral fibres are often present in cast-off industrial plants but they show a microscopy appearance easy to distinguish from asbestos fibres.

PROBLEMS CONCERNED WITH THE NATURAL PRESENCE OF ASBESTOS

L. Bologna¹, C. Cazzola¹, C. Clerici², E. Lauria¹, A. Salerno¹, M. Wojtowicz¹

¹ ARPA Piemonte, Polo Amianto, Grugliasco (TO), Italy

² Politecnico di Torino, Dipartimento di Ingegneria del Territorio dell'Ambiente e delle Geotecnologie, Torino,), Italy

Gli impieghi industriali e gli effetti nocivi degli "amianti", come definiti dall'insieme delle normative internazionali, sono da tempo acclamati.

La Legge 257/92 ha attivato meccanismi tali da portare alla definitiva dismissione dell'amianto. Premesso che sono da ritenersi ininfluenti, nel presente contesto, gli effetti prodotti sia dall'art. 4, comma 29, della Legge 9/12/98, che, previa autorizzazione, ha consentito fino al 31/10/2000 l'importazione di 800 kg/anno di amianto sotto forma di treccia e di materiale per guarnizioni, sia dall'art. 16 della Legge 128/98 "Disposizioni per l'adempimento di obblighi derivanti dalla appartenenza dell'Italia alle Comunità Europee", si deve osservare che, almeno formalmente, nell'aprile del 1994 è cessata ogni commercializzazione di amianto o di prodotti contenenti amianto. In altri termini la predetta norma ha fatto sì che fossero impediti nuove immissioni di amianto, di origine antropica, sul territorio nazionale.

Minor attenzione, in prima istanza, è stata posta dal legislatore alle problematiche igienico-sanitarie derivanti dall'amianto e dagli altri silicati fibrosi, non definibili amianto, presenti in natura.

Escluse alcune indicazioni contenute nella Legge 257/92 (censimento dei siti interessati da attività estrattive e predisposizione di programmi per la relativa dismissione) e nel D.P.R. 8/8/94 (censimento dei siti estrattivi di pietre verdi) fino al marzo 2003, l'unico atto normativo che trattava, seppure in modo limitato, la problematica dell'amianto naturale era l'allegato 4 al D.M. 14/5/96 (criteri di classificazione ed utilizzo delle pietre verdi). E il D.M. n° 101 del 18 marzo 2003 del Ministero dell'Ambiente e Tutela del Territorio, emanato in forza dell'art. 20 della Legge n° 93 del 23/3/01, che focalizza l'interesse. È disposta la mappatura della presenza di amianto naturale sul territorio nazionale, con contestuale indicazione dei siti che necessitano di interventi di bonifica urgenti. L'indice di priorità, definito sulla base di specifiche procedure, tiene conto di parametri quali: estensione del sito, distanza da recettori sensibili, tipologia del materiale contenente amianto, coinvolgimento del sito in lavori di urbanizzazione, dati epidemiologici. L'univocità dei criteri di priorità, sull'intero territorio nazionale, è garantita dal documento, predisposto da apposito gruppo di lavoro interregionale, approvato dalla "Conferenza dei Presidenti delle Regioni e delle Province Autonome" in data 29/7/2004.

Ricordato, infine, che il D.M. n° 101 del 2003 prevede la suddivisione dei siti in categorie, oggetto della presente memoria sono quelli appartenenti alla categoria "presenza naturale", ovvero quella inerente

- gli ammassi rocciosi, caratterizzati dalla presenza di amianto,
- le attività estrattive, in coltivazione o dismesse, di lavorazione di rocce e minerali con presenza di amianto;
- le attività estrattive, in coltivazione o dismesse, di lavorazione di rocce e minerali privi di amianto, ma in aree indiziate per la presenza l'amianto.

Il Piemonte è una delle regioni maggiormente interessate dalla presenza naturale di amianto, sia di serpentino (crisotilo), sia anfibolico (tremolite d'amianto, actinolite d'amianto, antofillite d'amianto, ai sensi della Direttiva 2003/18/CE). Tra le diverse aree interessate si ricordano:

le Valli di Lanzo, ed in particolare Balangero, con la presenza dell'ex sito minerario "S. Vittore" in cui si estraeva crisotilo a fibra corta e dove è possibile riscontrare altresì balangeroite; fibra su cui sempre più si discute anche a causa del suo contenuto di ferro;

l'area del comune di Trana in Val Sangone, ove è presente una cava di serpentino, ormai dismessa, con "massiva" presenza di tremolite;

l'area dell'ex miniera di amianto di Casteldelfino in Val Varaita, ove oltre al crisotilo è stata riscontrata la presenza di altre fibre tra cui la carlosturanite;

l'alta e la bassa Val Susa, dove i lavori per le olimpiadi invernali del 2006 e le attività di studio finalizzate alla realizzazione della TAV hanno portato alla ribalta una realtà, sebbene nota, non sufficientemente indagata;

la Val Lemme, ove le indagini legate all'apertura di una nuova miniera ed alle opere connesse (realizzazione di un acquedotto) hanno evidenziato la presenza di tremolite d'amianto.

Lo studio e la caratterizzazione di questi siti, la cui significatività è illustrata nei rilievi fotografici appresso riportati, non possono prescindere dai seguenti aspetti:

- livelli di concentrazione di fibre in aree in cui la presenza di amianto è da tempo conclamata;
- livelli di esposizione dei lavoratori e della popolazione nell'ambito di attività edili effettuate in aree con certa o sospetta presenza di amianto;
- presenza di altri silicati fibrosi, con caratteristiche chimico-fisiche simili a quelle degli amianti normati.

Per quanto attiene i primi due aspetti, premesso che in assenza di stress meteorologici e antropici, i valori di concentrazione sono generalmente inferiori ad 1 fibra/l, si sono osservati, causa l'azione degli agenti atmosferici e/o antropici (attività di scavo condotte con modalità inadeguate), innalzamenti significativi. Ad esempio, in un'area caratterizzata dalla presenza di affioramenti di tremolite molto friabile, le concentrazioni di fibre aerodisperse di amianto riscontrate in assenza di attività antropiche erano inferiori ad una fibra/litro; campionamenti successivi a lavori di scavo hanno evidenziato in prossimità del cantiere concentrazioni fino a 8,6 ff/l.

Relativamente al terzo aspetto, osservato che è usuale riscontrare in campioni di roccia o terreni asbestiferi fibre non classificabili amianto secondo l'attuale normativa, ma che hanno composizione e morfologia simile a quella degli amianti normati, tralasciate le difficoltà di ordine analitico non sempre risolte, è necessario interrogarsi sulla loro nocività.

Al fine di limitare esposizioni ad amianto, anche occasionali, è necessario quindi, oltre alla puntuale identificazione e registrazione dei siti, prevederne la successiva "gestione" da parte dell'amministrazione comunale interessata, con il coinvolgimento e la collaborazione di tutti gli enti a cui la normativa vigente attribuisce l'onere di presiedere alla tutela del territorio ed alla salvaguardia dei lavoratori. Si ritiene che le aree interessate debbano soggiacere a specifici vincoli urbanistici e che sia necessario predisporre specifiche procedure, condivise da tutti gli enti interessati, per l'emissione del parere igienico sanitario, indispensabile all'ottenimento delle concessioni edilizie. È, inoltre, auspicabile il diretto coinvolgimento delle amministrazioni comunali nel controllo dei cantieri interessati dalla presenza di minerali asbestiferi.

Se gli aspetti sanitari sono da considerarsi prioritari, non si devono tralasciare quelli sociali. Osservato che, ormai, è patrimonio diffuso la conoscenza sugli effetti nocivi sull'amianto, è doveroso fornire tempestivamente la più ampia informazione alle popolazioni interessate.

Si è dell'avviso che una corretta informazione eviterà l'insorgenza di inutili e pericolose tensioni sociali come più volte riportato dagli organi di stampa. In considerazione dell'accresciuta attenzione alle problematiche ambientali, è necessario che i cittadini vengano informati anche su tutti i provvedimenti adottati dalla pubblica amministrazione a salvaguardia della loro salute, quali ad esempio azione di messa in sicurezza, protocolli operativi a cui attenersi nel caso di esecuzioni di lavori edili. Quest'ultimo punto si ritiene fondamentale considerato che la mancanza di normativa specifica di riferimento determina comportamenti e/o modalità operative non appropriate, in grado di determinare massiva esposizione non solo degli operatori direttamente interessati, ma anche della popolazione residente.



Val Lemme, sponda torrente con presenza di tremolite



Val Susa, affioramenti su dehor di un bar (attualmente già "bonificato")

INVOLVEMENT OF OXIDATIVE STRESS AND CYCLOOXYGENASE IN THE EFFECTS INDUCED BY THE ASBESTOS-LIKE FLUORO-EDENITE FIBRES

V. Cardile¹, AM. Panico², L. Lombardo¹

¹Department of Physiological Sciences, University of Catania, Italy

²Department of Pharmaceutical Sciences, University of Catania, Italy

Some years ago, in an epidemiological study on mortality for malignant pleural neoplasm in Italy (1) it was found that some subjects who resided in Biancavilla, a town in eastern Sicily located in the Etna volcanic area, were diagnosed with malignant pleural mesothelioma, a rare neoplastic form caused by occupational, domestic, or residential asbestos exposure. These residents, for whom a diagnosis of pleural mesothelioma had been made, never had any relevant exposure to asbestos during their professional life. The results of an environmental survey, which was preliminarily conducted by the Istituto Superiore di Sanità and by the Dipartimento di Scienze della Terra dell'Università di Roma "La Sapienza", suggested that a possible cause for asbestos exposure of the Biancavilla population was the stone quarries present in Monte Calvario (2). This is located on the south-west side of the Etna volcanic complex, north-east of Biancavilla (Catania). The materials extracted from the quarries are widely used in the local building industry and contain large quantities of fibrous amphibole, which is, together with serpentines, one of the two groups of asbestos minerals (fibrous silicates) known. A detailed crystal-chemical investigation on the amphibole found in Biancavilla allowed to better define it as the new fibrous amphibole fluoro-edenite [ideal formula: $\text{NaCa}_2\text{Mg}_5(\text{Si}_7\text{Al})\text{O}_{22}\text{F}_2$], which occurs prevalently as acicular crystals and as fibres in the rock cavities of the whitish and grey-red altered benmoreitic lavas (3)

Therefore we planned a systematic investigation in order to understand whether fluoro-edenite present in Biancavilla was able to modify the normal cell metabolism, in relation to the development of the high incidence of cancer of the respiratory tract among the population. These our previous results showed that fluoro-edenite may induce functional modifications and affect some biochemical parameters in human lung fibroblasts, human lung alveolar epithelial cancer cell line A549 and monocyte-macrophage cell line J774 in a concentration and time dependent manner, indicating fluoro-edenite as a DNA damaging agent. This damage seems to be mediated by reactive oxygen species (ROS) and nitric oxide (NO[•]) generation (4,5) demonstrating that inflammatory disorders appear to increase the risk for lung cancer induced by fluoro-edenite probably by the involvement of reactive species. Moreover, other studies on effects of the fluoro-edenite in lung epithelial cells demonstrated that this new-identified amphibole interferes with epithelial cell physiology, by reducing the proliferation rate and increasing the release of the pro-inflammatory cytokine IL-6, one of the main mediators of asbestos-induced pathophysiological response (6). In the study of carcinogenesis, another highly significant point is the relationship between angiogenic factor production and tumour development. Cyclooxygenase (COX) is a well-known enzyme that catalyses the conversion of arachidonic acid to prostaglandins (PGs) in the cells. Two different isoforms have been discovered, COX-1 and COX-2, that catalyse the same chemical transformation but have a different genetic expression. While constitutive COX-1 is present in most mammalian tissues and mediates the synthesis of PGs required for many physiological functions such as maintenance of gastric and renal functions, vascular homeostasis, COX-2 is mainly induced in response to many pro-inflammatory stimuli, cytokines, growth factors and

mitogens. Moreover, COX-2 is up-regulated in several human tumours associated with increased production of PGs, which prove to be important in cancer pathogenesis since they affect mitogenesis, cellular adhesion, immune surveillance and apoptosis. Therefore, products of arachidonic acid metabolism are critical participants in the development of inflammatory responses after infection or tissue injury. Prostaglandin E₂ (PGE₂) is one of the most studied mediators of this process.

In this study, we investigated the involvement of COX-2 and PGE₂ in the cytotoxic effect and DNA damage caused by fluoro-edenite in monocyte-macrophage cell line J774. Alveolar macrophages, in fact, occupy a key position in mediating the interaction between inhaled particulates and various cell types, such as lymphocytes and fibroblasts, through the release of a wide variety of inflammatory and growth-mediating factors, as well cytokines.

The J774 cells, a mouse monocyte-macrophage tumour cell line, were cultured in Dulbecco's modified Eagle's medium (DMEM) containing 10% fetal calf serum, 4.5 g/L glucose, 1 mM sodium pyruvate, 100 U/ml penicillin, 100 µg/ml streptomycin, and 25 µg/ml fungizone (Invitrogen, UK) and incubated at 37°C and 5% CO₂. Fluoro-edenite from Biancavilla was added in culture medium of the J774 cells at concentrations of 5, 50 and 100 µg/ml for 24, 48, 72, and 96 h before cell harvesting. The expression of COX-2 was evaluated by Western blot analysis using primary mouse monoclonal COX-2 antibody (Cayman Chemical) and rabbit polyclonal α-tubulin antibody (Sigma) diluted (1:1000) in TBST. Antibodies were detected with horseradish peroxidase-conjugated secondary antibody using the enhanced chemiluminescence detection Supersignal West Pico Chemiluminescent Substrate (Pierce). The bands were measured densitometrically and the relative density of the bands was calculated based on density of α-tubulin band in each sample. The values were expressed as arbitrary densitometric units corresponding to signal intensity.

The concentration of PGE₂ was measured in the culture media by enzyme-linked immunosorbent assay (ELISA) (Kit Biotrak PGE₂ Amersham Pharmacia Biotech) according to the manufacturer's instructions. The optical density of each sample was measured with a microplate spectrophotometer reader (Titertek Multiskan, Flow Laboratories) at λ= 450 nm within 30 min.

Each experiment was repeated at least three times in triplicate and the mean ± SEM for each value was calculated. Statistical analysis of results was performed using Student's t-test and one-way ANOVA by the statistical software package SYSTAT, version 9 (Systat Inc., Evanston IL, USA). A difference was considered significant at P < 0.01.

This study investigated the effects in the time of new fibrous amphibole fluoro-edenite on the *in vitro* generation of prostaglandin (PG) biosynthesis and on the gene expression and protein synthesis of one key enzyme in the inflammatory process, inducible cyclooxygenase 2 (COX-2), in fluoro-edenite treated mouse monocyte-macrophage J774 cells, frequently employed in the evaluation of the degree of cytotoxicity to alveolar macrophages of various silica dusts (7). Figures 1 and 2 show the effects of fluoro-edenite on COX-2 and PGE₂ synthesis, respectively. As expected, basal COX-2 and PGE₂ levels of untreated control cultures were low. On the contrary, fluoro-edenite at 5, 50 and 100 µg/ml for 24, 48, 72 and 96 h has been demonstrated significantly to increase COX-2 and PGE₂ productions in concentration- and time-dependent manner. In particular, fluoro-edenite at 50 µg/ml for 96 h increased COX-2 and PGE₂ synthesis by control mean 13.5 and 8.3 times, respectively. At 100 µg/ml for 96 h the COX-2 and PGE₂ increase became 17.3 and 9.16 times with respect to the control values, respectively.

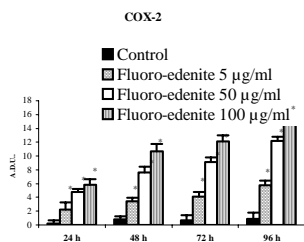


Figure 1 - Expression of COX-2

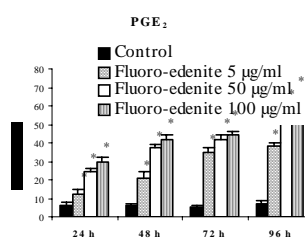


Figure 2 - Concentration of PGE₂

In summary, the present study investigated the involvement of COX-2 and PGE₂ in fluoro-edenite-induced genotoxicity in J774 cells. Our studies clearly demonstrate that oxidative stress and COX-2 activity appear to play a role in the development and progression of mesothelioma induced by fluoro-edenite. The overall data provides convincing evidence that oxidative stress and inflammatory factors mediate the fluoro-edenite induced carcinogenesis.

- [1] A. Gianfagna, L. Paoletti, P. Ventura, *Eur. J. Mineral.* 18, 117-119 (1997).
- [2] L. Paoletti, D. Batisti, C. Bruno, C., M. Di Paola, A. Gianfagna, M. Mastrantonio, M. Nesti, P. Comba., *Arch. Environm. Health*, 55, 392-398 (2000).
- [3] A. Gianfagna, R. Oberti, *Am. Mineral.* 86, 1489-1493 (2001).
- [4] V. Cardile, L. Proietti, AM. Panico, L. Lombardo, *Oncol Reports*, 12, 1209-1215 (2004).
- [5] V. Cardile, M. Renis, C. Scifo, L. Lombardo, R. Gulino, B. Mancari, AM. Panico, *IJBCB*, 36, 849-860 (2004).
- [6] S. Travaglione, B. Bruni, L. Falzano, L. Paoletti, C. Fiorentini, *Toxicol in Vitro*, 17, 547-552 (2003).
- [7] A. Shukla, M. Gulumian, T.K. Hei, D. Kamp, Q. Rahman, B. Mossman *Free Radical Biol. Med.* 3, 1117-1129 (2003).

DETERMINATION OF ASBESTOS IN VINYL FLOOR TILES BY FT-IR TECHNIQUE

P. Di Pietro^c, M. Campanella^c, C. Pierannunzi^c, M. D. Marcozzi Rozzi^c

c A.R.T.A. Agenzia Regionale per la Tutela dell'Ambiente, Dip. Provinciale di Teramo, Centro Regionale di Riferimento per l'Amianto (C.R.R.A.), P.zza Martiri Pennesi 29, 64100 Teramo, Italy. E-mail: p.dipietro@artaabruzzo.it, Fax: +39 0861 2565528; Tel. +39 0861 2565545

To day, the use of asbestos is forbidden in several technologically advanced countries. A material containing more than 1 wt% asbestos is classified as asbestos containing material (ACM) by the Environmental Protection Agency (EPA) and in Italy by D.L. 277, 15/8/1991.

However, the Italian law (DM. 6/9/94) establishes as reference methods for the quantifications of asbestos in ACM: X-ray powder diffraction (XRD), using the method of the silver filter, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscope (SEM).

The analysis of ACM continues to be an important function in protecting the public health, and XRD is one of the best method for quantitative analysis of asbestos. Unfortunately some mineral can interfere with the XRD analysis. Kaolinite, a relatively common industrial mineral, is a major interference in XRD analysis of asbestos because of the overlap of the two patterns.

On the other hand the SEM-EDS analysis is a good technique for the qualitative and semi-quantitative investigations of asbestos, but this have also too limits for the quantitative determination of asbestos in ACM.

In this communication the authors propose an analytical method for the qualitative and quantitative determination of asbestos in vinyl floor tiles using FTIR technique.

The XRD analysis of vinyl floor tiles places a series problems for the presence of kaolinite that can mask the peaks of chrysotile.

The powdered samples were carefully mixed with 200 mg of KBr infrared grade and pellettized.

The pellets were stored at 150°C for 10 minutes before processing.

Infrared spectra were registered from 4000 to 400 cm⁻¹ and the quantitative determination of asbestos carried out using one calibration curve ranging from 1.0% to 12.0%.

FTIR analysis carried out on conventional instrument allow to determine amount of chrysotile in the sample using a calibration curve using a small amounts of material.

This analytical method replies to the request of several public institutions and private companies for an appropriate quantitative determination of fibres of chrysotile in different type of vinyl materials.

POLYCRYSTALLINE FIBRE SIZE DISTRIBUTION BY SEM

C. Fanizza¹, G. Castellet y Ballarà², S. Casciardi¹, A. Marconi³

¹ISPESL, Dipartimento di Igiene del lavoro, Laboratorio Polveri e Fibre, Monte Porzio Catone, Roma, Italy

²INAIL, Istituto Nazionale per l'Assicurazione contro gli Infortuni sul Lavoro - Con.T.A.R.P. Centrale, Roma, Italy

³Istituto Superiore di Sanità ISS, Laboratorio di Igiene Ambientale, Roma, Italy

Man Made (synthetic) inorganic fibres are widely used through out the world, mainly as thermal and acoustic insulation products in both industrial and domestic applications. They include the well known fibres manufactured from glass, natural rock, minerals or readily melted slags (man-made vitreous fibres) and the recently developed class of polycrystalline fibres (oxide and non-oxide) [1] [2]. This last type of fibres in the recent years has been introduced in a wide number of high-temperature applications. Commercial polycrystalline oxide fibres are produced by spinning and pyrolyzing chemically-derived precursors. These chemical processes are commonly referred to as sol-gel or metal-organic processing. Such fibres are constituted mainly from alumina (Al₂O₃), mullite (3 Al₂O₃-2SiO₂) and zirconia (ZrO₂). The non-oxide fibres are polycrystalline SiC fibres or multiphase (amorphous or crystalline) combinations of boron (B), carbon (C), nitrogen (N), titanium (Ti) or silicon (Si) [3]. Commercially useful characteristics of most of these materials are high strength and excellent high-temperature resistance up to 1700°C [3] [4]. The International Agency for the Research on Cancer (IARC) currently classifies both refractory ceramic fibre (RCF) and polycrystalline fibres as Category 2B "Possible Human Carcinogen" [5]. Polycrystalline fibres are not covered by the directive 97/69/EC, which actually includes only vitreous, but not polycrystalline fibres [6]. Despite the increasing use of these fibres, still very few are the studies providing details of the characteristics that may be relevant for the potential exposure and for the toxic effects.

In this work we studied the dimensional distribution of diameters of a sample of polycrystalline alumina fibres and compared its morphological features with those of RCF. Moreover the presence of crystalline components was checked by qualitative X-ray diffraction. The sample of polycrystalline fibre under examination belongs to the wide category of aluminosilicate fibres which is largely used in many applications, even in substitution of RCF, thank to high temperatures resistance, good chemical stability, improved creep resistance of these materials [3].

The morphological and dimensional analyses were conducted by scanning electron microscopy (SEM). A small amount of bulk material (about 100 mg) was crushed in a 32 mm diameter die at 12.4 MPa for 1 minute. The material was mixed and re-pressed at the same conditions. The material was removed from the die and suspended in 200 ml of water. After ultrasonic agitation, aliquots of the water suspension were filtered on polycarbonate membranes with 0.8 µm pore size. A quarter of the filter was attached to aluminium stub and analyzed by a SEM (LEO S 440) equipped with energy-dispersive X-ray analysis (Oxford Instruments INCA). The SEM calibration was checked using a certified calibration

specimen (SIRA SEM standard). The diameter of 300 fibres was measured at 10,000 magnifications (15 mm working distance, 20 kV accelerating voltage and slow scan rate). In addition to the diameter distribution of the sample, the length weighted geometric mean diameter (LWGMD) minus two standard errors was measured in order to test the value of the parameter indicated in the Directive 97/69/EC, applying the procedure of the European Chemical Bureau [7]. X-ray diffraction analysis was conducted after comminution of the sample, suspension in ethanol and deposition on silver filter in the form of very thin layer.

The diameter distribution of the sample is shown in Table I and in Figure 1.

Diameter (μm)	Fibre number
0 - 1	1
>1 - 3	30
>3 - 5	225
>5 - 7	36
>7 - 9	6
> 9	2

Table I: Polycrystalline fibre diameter distribution by SEM

In Table II are reported the main statistical parameters and the value of the LWGMD parameter.

X-ray diffraction results, illustrated in Figure 2, showed the presence of peaks of various crystalline phases, among which are depicted the two characteristic peaks of mullite at 16.43 and 26.30 2-theta degrees.

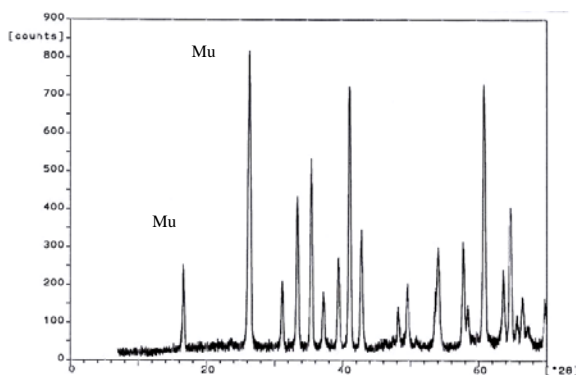


Figure 2 – DRX spectrum of polycrystalline fibre sample. Mu: mullite

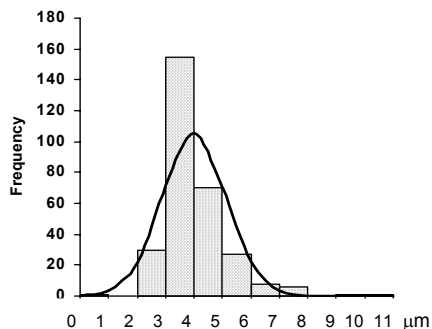


Figure 1-Diameter distribution of the sample

Geometric Mean (GM) (μm)	3,86
Standard Deviation (SD)	1,13
Geometric Standard Deviation (GSD)	1,32
Standard Error (SE) (μm)	0,06
LWGMD – 2SE (μm)	3,74

Table II: Descriptive statistics for calculation of LWGMD (by SEM)

In Figure 3a is shown the characteristic conchoidal shape of the surface at the point of fracture for vitreous RCF. On the contrary polycrystalline fibres (fig.3b) showed a rough surface constituted of relatively fine grains with size of about 0.5 μm or less.

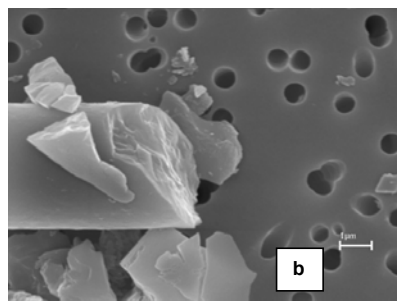
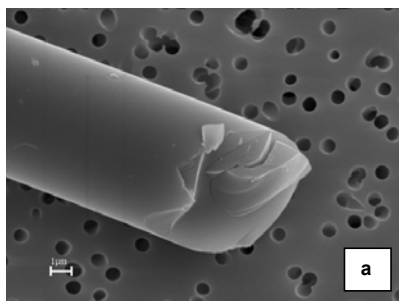


Figure 3- Electron micrographs of fracture surfaces of: a) refractory ceramic fibre; b) polycrystalline fibre. Bar 1 μm .

The polycrystalline fibre sample examined showed a very narrow diameter distribution around 3-5 μm , with a LWGMD of 3.86 μm (and a LWGMD-2SE of 3.74 μm) which is significantly greater than the characteristic diameter of RCF, but still in the respirable range.

This property and the nature essentially crystalline, as resulted from the X-ray analysis, indicate that this material should be treated with caution, because it has the potential to be even more biopersistent than RCF fibres.

The morphological features of the fractured surfaces of polycrystalline fibres, if confirmed by a larger number of analyses, could help in the identification and discrimination of this type of fibres.

The increasing use of polycrystalline fibre should be treated with care and appropriate precautions should be adopted during their manipulation.

References

- [1] BROWN S.K., *Am. Ind. Hyg. Assoc. J.*, 53, (1992)
- [2] M.A. MOORE, P.M. BOYMEL, L.D. MAXIM, J. TURIM, *Regul. Toxicol. Pharmacol.*, 35, 1-13 (2002)
- [3] COMMITTEE ON ADVANCED FIBERS FOR HIGH-TEMPERATURE CERAMIC COMPOSITES, *Ceramics Fibers and Coatings. Advanced materials for the twenty-first century, Publication NMAB-494 National Academy Press Washington, D.C.* (1998)
- [4] T. ISHIKAWA, *Intern. J. Mat. Prod. Technol.*, 16, 180-188 (2001)
- [5] (IARC), *Monographs on the Evaluation of Carcinogenic Risks to Humans: Man-Made Mineral Fibers, IARC Monographs, Volume 81, International Agency for Research on Cancer, Lyon, France* (2002)
- [6] Commission Directive 97/69/EC of 5 December 1997 adapting to technical progress for the 23rd time Council Directive 67/548/EEC.
- [7] ECB-JRC, Ispra, Thesting Methods: Draft - 4 rev.2 (2003) <http://ecb.jrc.it/testing-methods/>

QUANTITATIVE ANALYSIS OF CHRYSOTILE IN ANTIGORITE-SERPENTINITES USING SPECTROSCOPIC AND THERMAL ANALYSIS

Chiara Groppo¹, Roberto Compagnoni¹, Giorgio Lesci², Guido Fracasso², Norberto Roveri²

¹ Dept. of Mineralogical and Petrological Sciences – University of Torino, Italy.

² Dept. of Chemistry "G. Ciamician" – University of Bologna, Italy

Microscopic and X-ray diffractometric techniques are unsuccessfully applied in the quantitative determination of chrysotile (Ctl) in antigorite (Atg) serpentinites.

FTIR spectroscopy and TGA-DTA analyses have been applied to quantify Ctl in Atg serpentinites from the western Alps. Ctl-Atg mixtures have been used to simulate natural Atg serpentinite rocks with different amounts of Ctl fibers in the whole range of composition. We have analysed fitting of the adsorption bands at 3690, 3646 cm^{-1} and 3699, 3678, 3570 cm^{-1} characteristic of Ctl and Atg respectively, obtaining a linear plot of the 3690 cm^{-1} intensity Vs %wt of Ctl. The same samples analysed by TGA-DTA technique have allowed to obtain a calibration curve of the ΔH Ctl / ΔH Atg dehydroxylation as a function of the Ctl amount in the samples.

These two correlation plots obtained by FTIR spectroscopy and TGA-DTA analyses allow to evaluate the wt% amount of asbestos fibres in antigorite serpentinites with a resolution very close to 0.1% wt.

LONG-TERM ASBESTOS MONITORING IN LIFE AND PROFESSIONAL ENVIRONMENTS OF SELECTED ITALIAN SITES

A. F. Gualtieri¹, S. Ferrari¹, A. Ricchi², E. Foresti³, G. Lesci³, N. Roveri³, M. Mariotti⁴, G. Pecchini⁵

¹ Dipartimento di Scienze della Terra, Università degli Studi di Modena e Reggio Emilia, Italy

² Dipartimento di Sanità Pubblica, Azienda USL Modena Città, Modena, Italy

³ Dipartimento di Chimica "G. Ciamician" Alma Mater Studiorum, Università di Bologna, Bologna, Italy

⁴ Dipartimento di Sanità Pubblica, Azienda USL Bologna Città, Bologna Italy

⁵ ARPA, Sezione Provinciale di Reggio Emilia, Reggio Emilia, Italy

Air-dispersed particulate material, and especially asbestos fibres which represent a hazard for the human health, may originate from different media (bulk materials such as ACM=asbestos containing materials in civil or industrial buildings, quarries or mines, work or life private/public buildings, soils, water, etc). Consequently, it is of paramount importance to monitor the presence of particulate not only in air but also in other media such as water and soils (the so called *fall-out* particulate) to carefully assess the real levels of exposure risk in life and work environments. Of course, the qualitative detection of particulate and especially asbestos requires specific sampling, analytical methods and protocols. The aim of this project, started this year and granted by the Fondazione Cassa di Risparmio di Modena (Modena, Italy), is the long-term asbestos and inorganic particulate (with a special care to PM10 particulate) monitoring in life and professional environments of selected Italian sites. Table 1 reports the location and main characteristics of the sites selected for the investigation.

Table 1. Location and main characteristics of the sites selected for the ALS investigation.

District/Nr site	Site	Main characteristics
Reggio Emilia (1)	Temporary waste deposit including cement-asbestos materials in a city highly industrialized area	possible source of particulate dispersion in air
Modena (2)	Civil area nearby the ceramic industrial area in Sassuolo, the main ceramic pole in the world	blank
Modena (3)	Ceramic factory in Pavullo, a mountain area (Modena Appenine)	possible source of particulate dispersion in air
Modena (4)	Ceramic factory in Sassuolo	possible source of particulate dispersion in air
Modena (5)	Monitoring station in a very clear mountain area (Monte Cimone, Modena Appenine)	blank
Bologna (6)	Train Station of Bologna	possible source of particulate dispersion in air
Bologna (7)	Civil University area nearby the center of the city (Dipartimento di Chimica, Bologna)	blank
Reggio Emilia (8)	Recreational building with the cover made of cement-asbestos nearby a primary school in the small village of Roncocesi (Reggio Emilia)	possible source of particulate dispersion in air/blank

Work and life environments with different characteristics (typology of the asbestos material and associated level of risk, geographical position, activity within and nearby the monitored site, closeness to public buildings, etc) were selected within the Bologna, Modena and Reggio Emilia Provinces (Italy) and kept monitored for about one year to investigate the activity of the asbestos fibres and other inorganic particulate during different seasons and environmental/climate conditions. For each monitoring site selected for its potentiality to be a source of particulate dispersion in air, a corresponding blank (presumably with zero or low probability of particulate dispersion) site has been monitored in order to collect also the background dispersion values. For example, the monitoring of a Ceramic factory in Sassuolo (Modena, Italy) whose production sheds have roofs made of cement-asbestos (see Figure 1 which shows the high flux air sampler, indicated by the arrow, about 1 m away from the cement-asbestos roof at the Ceramic production site) is accompanied by the monitoring of a blank site, a civil building about 1 Km away from the production site.

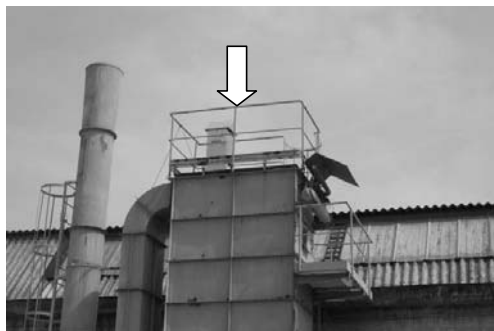


Figure 1 – The cement-asbestos roof at monitoring site 4. For each site, different monitoring strategies were utilized.

Monitoring was conducted in continuous mode for 1 week and is repeated 4 times a year (spring, summer, autumn, and winter time). For the production sites, the monitoring spot is located very close to the dispersions source (such as the cement-asbestos roof) and about 50 m away from it to assess, if any correlation between the particulate concentration/nature and the distance from the dispersion source exists. The monitoring of the airborne dispersed particulate was possible using an especially modified high flux volumetric (ca. 1 m³ per min) area air sampler (shown in Figure 2) and large cellulose filters (A4 paper size). Given the high air flux, filters tend to be quickly over-saturated and have to be changed every second day. The fall out particulate is collected in a 1 m² wide collector filled with water which simulate a water source. Water samples are then filtered to separate the solid fraction and dried to be investigated with the lab experimental techniques. Samples of the surface soil are also collected in the proximity of the monitoring sites to assess the nature and concentration of the particulate deposited in a long term. The analysis of the collected samples was possible using bulk (X-Ray powder diffraction with advanced methods and the Rietveld method [1-3], microdiffraction, and FTIR) and microscopic techniques (SEM, TEM; optical microscopy) in the attempt to determine the nature, meso-microstructure and density of the inorganic particles. The analytical protocol established for this project accomplishes different steps:

- Quali-quantitative XRPD, SEM and optical microscopy of the raw soils and water fall out samples
- Separation of the particulate from the filter by sonication in acetone
- Quali-quantitative XRPD, SEM and optical microscopy of the separated particulate samples
- Thermal treatment at 500 °C for 1 h of all the filters, raw soils and water fall out samples

- Quali-quantitative XRPD, SEM and optical microscopy of all the thermally treated residue of the filters, raw soils and water fall out samples
- Wet separation/enrichment of asbestos using the Appiani levigator method of all the thermally treated residue of the filters
- Quali-quantitative XRPD, SEM and optical microscopy of asbestos residue obtained by the wet treatment using the Appiani levigator method
- DSC+TA, FTIR, and TEM analyses on selected samples which require further inspection

Because we are still at the monitoring stage (the autumn shift will be accomplished at the end of November), we can present only preliminary results. We have now focussed our attention on site 4, the Ceramic plant.

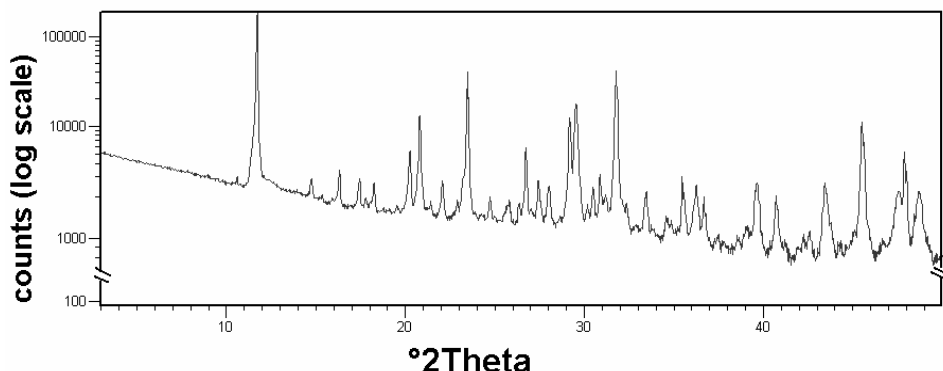


Figure 2. XRPD pattern of the fall-out particulate deposited in water, site 4a, Spring shift.

The analysis of the samples collected during the Spring and Summer shifts right under the cement-asbestos roof (site 4a) and 50 m away from it (site 4b) have shown that the phase composition of the particulate is extremely heterogeneous with a variety of natural and synthetic phases typical of the raw materials used in the ceramic industry (see for example the powder pattern of fall-out particulate deposited in water in a week during the Spring shift. The reflections of at least 10 different phases are present (halite, quartz, gypsum, calcite, cristobalite, graphite, albite, spinel, mullite and zircon). Up to the time of the preparation of this abstract, no asbestos fibers were detected in the investigated samples relative to site 4a and 4b. Even the SEM investigation has shown a variety of particles of different nature but no asbestos.

[1] G. Falini, E. Foresti, M. Gazzano, A. F. Gualtieri, I. G. Lesci, G. Pecchini, E. Renna and N. Roveri, *J. of Environ. Monitoring*, 5(4), 654-660 (2003)

[2] E. Foresti, M. Gazzano, A.F. Gualtieri, I.G. Lesci, B. Lunelli, G. Pecchini, E. Renna, N. Roveri, *An. Bio. Chem.*, 376(5), 653-658 (2003)

[3] A.F. Gualtieri, G. Artioli, *Powder Diff.*, 10(4), 269-277 (1995)

NATURALLY OCCURRING ASBESTOS MINERALS FROM METAOPHIOLITES: RATIONALES FOR CUSTOM-DESIGNED ANALYTICAL CONSTRAINTS

Cortesogno L.¹, Gaggero L.¹, Marescotti P.¹, Robbiano A.²

¹ Department for the Study of Territory and its Resources (DIPTERIS), Università di Genova, Genova, Italy

² Studio Associato di Geologia Tecnica ed Ambientale, c.so Garibaldi 58/5, Chiavari (Genova), Italy

Few regions in Italy experience the occurrence of wide metaophiolite outcrops as Liguria. Two types of metaophiolites differentiated in the Apennine (eastward) and in the Alpine (westward) belt systems.

i) The Apennine nappe was affected by very low grade to low grade metamorphism; therefore ultramafic rocks are mostly constituted by chrysotile and lizardite serpentine polymorphs. Other potential asbestos minerals can occur in basic rocks (metagabbros and metabasalts) as needle-shaped to fibrous calcic amphiboles. In Apenninic serpentinites (east of the Levante – Ottone alignment towards Tuscany), chrysotile is generally associated with lizardite: ia) in massive serpentinites as aggregates of fibres (< 3 µm in length) occurring with dominant lizardite in bastites or in interlocking and hourglass textures; ib) in veined serpentinites either as serrate or weak aggregates of fibres, from 0.1 to some mm in length.

In the ia) case chrysotile can be dispersed only by mechanical grain size reduction, but single fibres are rare and their size hardly represent a danger. In case ib) fibres can be released either by mechanical grain size reduction and by routine quarry operations; in this case fibres abundance tend to be higher than in the bulk rock and easily concentrate in air or within muddy sediments and waters. Fibrous calcic amphibole from basaltic or gabbroic rocks in Apennine and Alpine ophiolites can be easily released only by milling.

ii) In the Alpine nappe, metaophiolites were re-equilibrated under several high-P/T conditions during subduction processes, and include amphibole-bearing eclogites, blueschist and greenschist facies rocks. The high P/T ultramafic

rocks are mostly constituted by massive to fibrous antigorite, crosscutted by lizardite and chrysotile veins. In particular, in serpentineschists outcropping between Genova and Savona, chrysotile appears associated with antigorite as weak fibres aggregates from 1 to 100 μm in length.

In the basic rocks the potential asbestos minerals are acicular to fibrous ferromagnesian, calcic, sodic – calcic, and sodic amphiboles. The latter fibrous amphiboles mostly occur within metabasalts, metagabbros, and eclogites. They can be both rock forming minerals (and therefore easily released only by milling or grinding operations) or vein – filling minerals, occurring as mm-sized aggregates of fibres: in the latter case simple friction or routine quarry operations can easily release asbestos.

Another potential asbestos-bearing rocks are ophicalcites that occur both in the Apennine and in the Alpine metaophiolites, showing different extent of carbonatation i.e. different situations of possible fiber release.

Finally, both in the Alpine and Apennine metaophiolites, either the massive rock bodies or the vein systems can host minerals with acicular to fibrous habit such as brucite, zeolites, Fe-Mg bearing phases (talc, diopside, hornblende) and sepiolite.

The wide distribution as well as the variety and extent of asbestos-bearing rocks make Liguria a significant case study for the evaluation of fibres dispersion either by natural events and processes (such as erosion/transport sedimentary cycle) or as a consequence of anthropic intervention that comprise quarrying operations, excavation for tunnel, foundations, and road constructions. At several occurrences, exceptionally high asbestos concentrations, due to mechanisms of selective concentration on the fine-grained mineral fraction, were evidenced in areas close to ophiolitic districts that underwent excavations or significant erosion processes.

All these situations are not specifically included in the Italian normative and are particularly difficult to characterize following the standard analytical procedures.

Current analytical, standard-based, methods accepted for industrial asbestos (such as IR-spectroscopy, SEM not equipped with quantitative, in situ analysis) have proved biased when applied to natural occurring asbestos, in particular amphiboles.

The identification of different serpentine polytypes on fine grained powders is a further problem; the most effective analytical methods for identification and semi-quantitative estimation is the X Ray powder diffraction (XRPD).

However, XRPD could over-assess the abundance of chrysotile due to difficulty in discriminating the size and the morphology of the mineral phase. In this case a cross-check involving XRPD analyses and optical microscopy, performed both on powders and/or on rock thin sections, is suggested.

As for amphiboles, the concentrations in milled powders can result slightly lower than the total amphibole abundance in the sample.

The identification of amphibole fibers (crocidolite and tremolite) can be adequately performed with the standard analytical procedures of the Italian normative.

On the whole, taking into account the morphometric features of asbestos, in case of massive natural samples from different geological occurrences the characterization under optical microscope (minero-petrographic investigations) is the most reliable method, whereas in case of fine grained and/or heterogeneous materials (soils), optical microscopy associated with XRPD analyses is particularly effective.

Several interpretative problems were recently raised due to the lack of more specific normative on (meta)ophiolites and related anthropic activities (quarrying, excavations, civil or industrial building, coast re-shaping etc.); the natural materials resulted better characterized by the sum of a standard-independent analytical methods, where also the operator-dependent component is minimized (such as XRPD), and optical microscopy analyses, whose results are dependent on the interpretation and experience of the analyst.

On the whole, some final recommendations to improve administrative procedure and get reliable analytical results, can be listed on the ground of our case-histories

1. Mapping of the concentrations of the natural background in ophiolitic districts (outcropping rocks, incoherent and stream sediments).
2. Monitoring of airborne asbestos fibers derived from activities in ophiolitic districts other than quarrying (road tracing, tunnels, building foundations etc).
3. Identification of sites for storage of asbestos-bearing tout venant, milling muds etc, where they do not raise the natural background concentrations.
4. Planning procedures for inertization of materials produced at point 3)
5. Definition of sampling procedures for quarried sites and possibility to select the most appropriate analytical procedures for materials used in "natural" environment such as coastlines and beaches.
6. Definition of appropriate normative and procedures for the characterization of asbestos-bearing materials derived from hill or river quarries and used within a natural geological cycle (fillers, beaches)

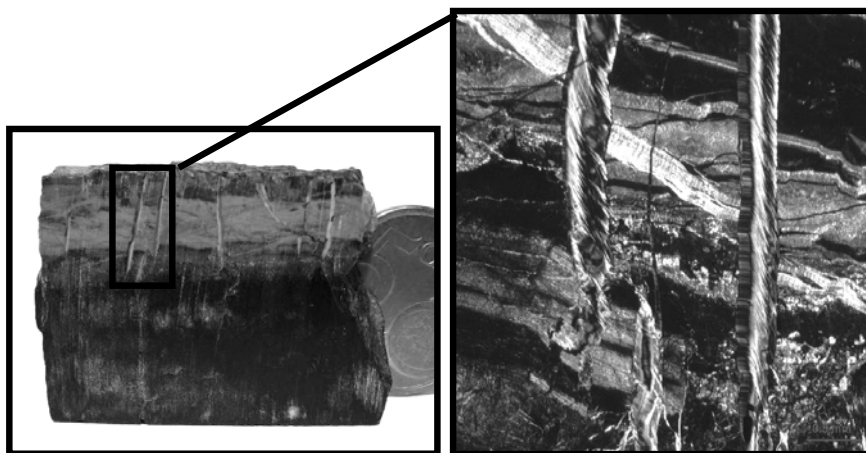


Figure 1 – Crosscutting generations of chrysotile – bearing fractures in Eastern Liguria serpentinites (Ponte Nuovo Quarry)

ASBESTOS SUBSTITUTIVE MATERIALS: ANALYTICAL PROTOCOLS FOR CLASSIFICATION OF MAN-MADE VITREOUS FIBRES AS CARCINOGENIC AGENTS

E. Incocciati, S. Massera, F. Nappi

INAIL CONTARP: Italian Workers' Compensation Authority, Risk Assessment and Prevention Central Technical Advisory Department – Rome, Italy

Man-made vitreous fibres (MMVF) are widely used in both civil and industrial ambit, because of their mechanical and heatproof characteristics, similar to asbestos' ones. According to a IARC Monograph [1], ceramic refractory fibres (FCR), a particular kind of MMVF, have been included in group 2B "possibly carcinogenic to humans", while the others have been considered as less dangerous materials.

In Italy the DM 1st September 1998 [2], acknowledging the Directive 97/69/CE, fixes criteria for classification, packing and labelling of MMVF. According to the Circular no. 4, 15th March 2000 [3], which contains the explanatory notes to this Decree, MMVF having casual orientation are divided, on the basis of their chemical composition, in mineral wool (labelled as R40¹ and R38) and FCR (labelled as R49 and R38).

These materials won't be labelled as R40 and R49 when they are made up of fibres having the D_{LG-2ES} (Length Weighted Geometrical Mean Diameter minus two Standard Errors) higher than 6 μm . The Enclosure 1 of the Circular 4/2000 provides a method to evaluate the D_{LG-2ES} , but it doesn't explain the modalities of samples preparation and fibres count, which can influence the evaluation of this parameter: this can lead to unreliable labelling of MMVF carcinogenicity, with important effects on both precautionary and insurance aspects.

In industrial hygiene scarcely repeatable methods are often adopted; sometimes they are suggested by the analyst's experience, who hasn't standardised and national or international shared procedures.

In the European Community a series of protocols for the evaluation of the D_{LG-2ES} is studied, in order to standardise this kind of measurement and to make different kinds of fibres peculiarities comparable.

The Draft 4 of the European Chemical Bureau [4] proposes a method to analyse fibrous materials using Scanning Electron Microscopy (SEM) to evaluate the D_{LG-2ES} ; furthermore operative modalities based on the use of PCOM (Phase Contrast Optical Microscopy) have been carried out [5, 6, 7, 8] but, in spite of the studies made and the proposals put forward, an official protocol for this kind of determination doesn't exist yet.

This paper reports experimental data collected by INAIL CONTARP industrial hygiene laboratory with the aim to check the best practice to classify MMVF, to draft an appropriate analytical protocol and to calculate the achievable repeatability level.

A batch of FCR samples coming from a pottery oven has been prepared according to two different comminution and drawing modalities. Fifteen samples have been prepared with a "dry procedure" while further six slides have been obtained following a "wet procedure". In all, 3 analysts have made 64 determinations over 21 slides. Both the procedures are described in table 1.

¹ R38: irritating to skin; R40: limited evidence of a carcinogenic effect; R49: may cause cancer by inhalation (D.M. 16/2/93 referred to Dir. 67/548/CEE).

Table 1: procedures adopted in sample preparation.

Phase	"DRY" procedure	"WET" procedure
Apparatus Equipment	Thin tip tweezers, slides and coverslips, triacetin, cutter, glass stick, heating plate, microscope and accessories in compliance with the D.Lgs. 277/1991 [9].	Thin tip tweezers, slides and coverslips, triacetin, cutter, isopropanol, 10 ml volumetric flask, stirrer, 25 mm diameter MCE membrane (por. 0,8 µm), acetone flash vaporisation system, glass filtration apparatus to take 25 mm diameter filters, heating plate, microscope and accessories in compliance with the D.Lgs. 277/1991, analytical balance.
Sampling	An aliquot of the core of the MMVF blanket is picked up with the tweezers.	An aliquot (50÷100 µg) of the core of the MMVF blanket is picked up with the tweezers.
Comminution	The sample is placed on a slide, mixed with 2 drops of triacetin and chopped up with the cutter for 8 minutes.	
Sampling	8-10 portions of the emulsion are picked up and moved on a second slide with the glass stick.	The emulsion is moved into the volumetric flask by washing the slide with isopropanol (fill the flask up to 10 ml).
Preparation	In order to obtain an homogeneous fibres distribution, the sample is homogenised with the glass stick adding 3 drops on triacetin.	After the stirring, the mixture is filtered with the glass apparatus on the MCE membrane.
Sealing	The sample is covered with a coverslip, placed on the heating plate for at least 15 minutes and sealed.	The filter is placed on a slide and cleared with acetone vapour. After the addition of three drops of triacetin the sample is covered with a coverslip, placed on the heating plate for at least 15 minutes and sealed.
Maintenance	Slides are carried and stored horizontally in order to avoid fibres migration.	
Analysis	Lengths and diameters of 200 fibres or pieces of fibres are measured using the Walton Beckett graticule at the magnification of 500 X.	

The D_{LG} -2ES has been calculated according to the equation reported in enclosure 1 of the Circular 4/2000 [3]:

$$D_{LG} - 2ES = \exp[\log D_{LG} - (2 \log \sigma_{LG} / \sqrt{n})] \quad [a]$$

where n is the number of the objects examined, σ_{LG} is the standard deviation (DS) of n measurements.

Measures of diameters have been processed according to the equation shown in the Draft 4 ECB too:

$$LWGM D - 2SE = e^{\frac{\ln D - 2SE}{D}} \quad [b]$$

with $LWGM D$: length weighted geometric mean diameter and SE : standard error, equal to DS/\sqrt{n} .

The equations [a] and [b] differ each from the other because the former needs the measure of object length L_i , being:

$$\log D_{LG} = \sum_i \log D_i \cdot L_i / \sum_i L_i$$

However, the two formulae can be considered conceptually equivalent being both based on logarithmic mean, respectively to base 10 and to base e .

Table 2 shows data of the "dry" and "wet" analysis processed according to the two different calculus methods (D_{LG} -2ES e $LWGM D$ -2SE).

Table 2: data processing of the analysis.

Parameter	"DRY" procedure		"WET" procedure	
	Circular 4/2000: D_{LG} -2ES	Draft 4 ECB: $LWGM D$ -2SE	Circular 4/2000: D_{LG} -2ES	Draft 4 ECB: $LWGM D$ -2SE
Mean value	3,40	3,25	3,76	3,78
Minimum value	2,34	1,86	2,77	2,86
Maximum value	4,37	4,44	4,83	4,91
Standard Deviation (DS)	0,49	0,56	0,43	0,48
Variation Coefficient (CV)	0,14	0,17	0,12	0,13

Despite the D_{LG} -2ES e $LWGM D$ -2SE mean values obtained over the samples prepared with the "wet" method are slightly higher than the other ones, it can be stated that measurement results don't depend on sample preparation procedures.

Among the several adaptable preparation procedures, only two have been tested in this study: in lack of specific laws in force or standardised methods, self done testing undertaken by laboratories are not only "lawful", but also in conformity with the contents of the Circular 4/2000.

As regards methods repeatability, comparable and numerically rather low DS can be associated to the results obtained from both procedures. It can be observed that following the "wet" preparation a more homogeneous fibre distribution can be obtained, as results from low magnification analysis (125 X). These samples are more suitable for the analysis because the fibres are not clumped, but they're well distributed on the filter.

The results obtained using both the ECB and the Italian Circular 4/2000 protocols aren't too different. The ECB method doesn't need the determination of fibres length: that's why, according to the adopted procedures, the characterisation may be carried out without evaluating fibres length.

The described work in progress is leading to the drawing up on a CONTARP internal protocol for risk assessment related to the managing of MMVF.

Moreover, it will be possible to assess the accuracy of the results through the statistical treatment of the data.

[1] International Agency For Research On Cancer. *IARC Monographs On The Evaluation Of The Carcinogenic Risk Of Chemicals To Humans*, 81 (2002).

[2] Decreto del Ministero della Sanità 1 Settembre 1998. G.U. 271 (1998).

[3] Circolare del Ministero della Sanità N. 4. G.U. 88 (2000).

[4] European Chemical Bureau. *ECB/TM/1(00) rev 2, Draft-4*, (2000).

[5] Marconi A., Chiamonte C., Castellet Y Ballarà G., Cacchioli E. *SYMPOSIA: I CONGRESSI DELLA FONDAZIONE MAUGERI*, 4: 185-190 (2000).

[6] Marconi A., Castellet Y Ballarà G., Cacchioli E., Fizzano M. R., Camillucci L., Campopiano A., De Blasi P. *ATTI 19° CONGRESSO NAZIONALE AIDII*: 70-74 (2001).

[7] Incocciati E., Massera S., Nappi F., Barreca F. *ATTI 22° CONGRESSO NAZIONALE AIDII*, 175-178 (2004).

[8] Bacci T., Sala O., Renna E., Pecchini G., FERDENZI P. *ATTI 22° CONGRESSO NAZIONALE AIDII*, 184-187 (2004).

[9] DECRETO LEGISLATIVO N. 277 in Supp. Ord. G.U. n. 200 (1991).

ANALYTICAL EVALUATION OF WASTES CONTAINING ASBESTOS AFTER INERTIZATION TREATMENT BY PYROLITIC PROCESS

Giovanni Pecchini⁽¹⁾, Alessandro F. Gualtieri⁽²⁾, Emilio Renna⁽¹⁾, Orietta Sala⁽¹⁾, Luigi Calzavacca⁽³⁾, Tiziana Bacci⁽¹⁾, Federica Paoli⁽¹⁾, Valeria Biancolini⁽¹⁾

⁽¹⁾ARPA, Sezione Provinciale di Reggio Emilia

⁽²⁾Dipartimento di Scienze della Terra, Università degli Studi di Modena e Reggio Emilia.

⁽³⁾Eco Studio - Aspireco, Gavardo Brescia

Wastes recovery efficiency have been slightly improved by Decree n.248 of 29/7/2004 on "Rules on determination and disciplines of recovery activities of products and goods of asbestos and containing asbestos" by defining processes and treatment able to bring to a complete transformation of crystallochemical features of asbestos.

Such treatments if properly applied allows to avoid the disposal of wastes in dumps. They also allow the reutilization of processed wastes. No adequate power plants suitable for the mentioned treatment presently exist in Italy.

Intense research activity is devoted to the start up of pyrolytic processes applied to wastes deriving from concrete/asbestos to be reutilized in environmental recovery. Decree n.248 reports characteristics of processed material which must be asbestos free and accompanied by mineralogical composition of final product.

Present paper propose an analytical protocol suitable for law need and able to guarantee safety conditions of wastes after crystallochemical transformation.

In order to verify such transformations analytical procedures adopted in qualified laboratories on asbestos analysis have been utilized. Pure chrysotile and concrete/asbestos samples have been analyzed by MOCF, DRX, SEM and FTIR after 2 hours heating at 600-700-800-900-1000 °C in muffle furnace. Some samples processed by pilot power plant by Aspireco have also been analyzed.

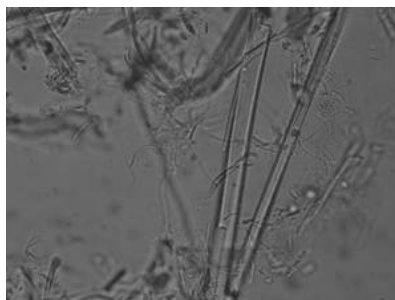
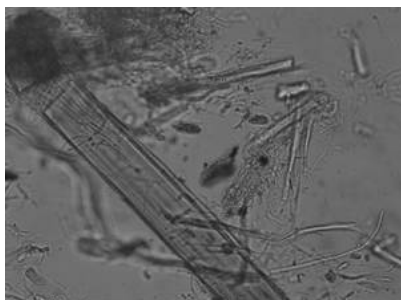


Figure 1-2. Chrysotile sample after pyrolytic treatment in pilot power plant.

Main high temperature transformations of asbestos containing materials are described as solid state deoxydrilization and recrystallizations (Gualtieri and Tartaglia, 2000). Thermal treatment of pure chrysotile evidences that after deoxydrilization at 800 °C starts a solid state transformation which brings to a complete recrystallization into silicatic-magnesiatic phases (forsterite and enstatite). After this transformation chrysotile loses fiber-asbestos characteristic and is not dangerous for health. Asbestos by pure tremolitic amphibole thermally processed at 1100 °C after deoxydrilization is completely transformed in diopside, enstatite and cristobalite. Flaked asbestos represented by chrysotile and processed at 1000 °C show that asbestos original characteristic is completely decomposed and three new phases of gehlenite, diopside and iron forsterite are crystallized. X ray diffractometry of concrete/asbestos constituted by prevailing chrysotile processed at 1100 °C evidence new phases deriving from chrysotile transformation such as prevailing gehlenite and diopside in a less extent. Quartz and hematite have also been found as residuals. SEM analysis of obtained materials evidence the inertization of fibrous phases which are transformed into irregular aggregates of neoformation crystals accompanied by loss of original dangerous character.

MOLP

Is the simplest technique which enables to verify optical properties of asbestos crystals.

Chrysotile processed at relatively low temperatures (600-700 °C) is still characterized by original colour and colour changes which completely disappear at higher temperatures evidencing the complete crystalline structure transformation.

DRX

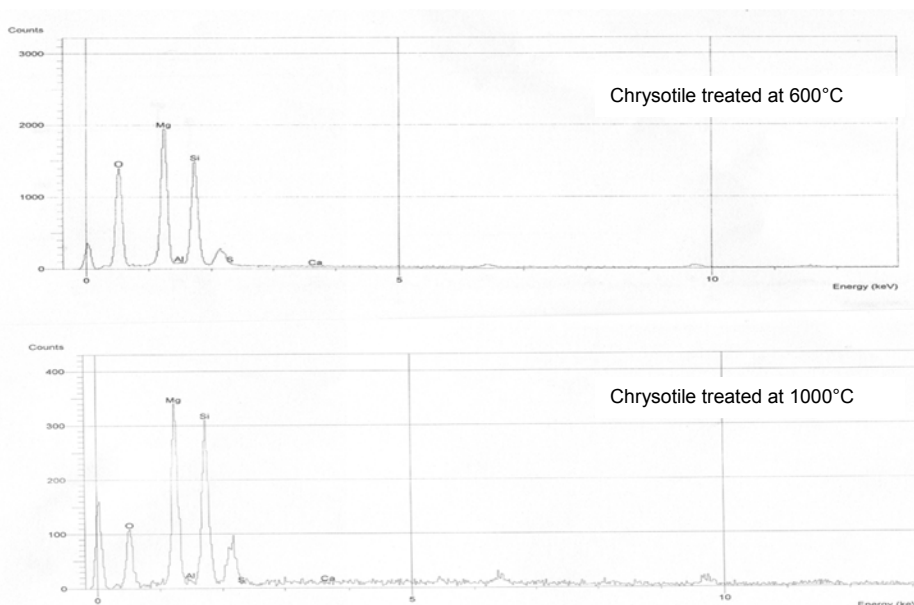
Main (12.1°) and secondary (24.3°) reflexed rays expressed as 2 Theta are recognizable on chrysotile and concrete/asbestos samples processed at 600-700 °C while are not visible on samples processed at temperatures higher than 800 °C. A detailed study on diffractogram allows to recognize new recrystallization phases.

SEM

Chrysotile fibers morphology tends to modify losing characteristic flexuous curves of chrysotile and assuming a rigid character closer to artificial mineral fibers. New recrystallized fibers tend to broke transversally differently to asbestos ones. Qualitative analysis of EDX spectra evidences an increasing oxygen loss related to increasing temperature of the sample.

FTIR

FT-IR spectrophotometry is a highly sensitive analytical method which allows to analyze samples in relatively short times and good repetitivity. Samples of KBr, chrysotile and concrete/asbestos have been grinded, transformed into tablets and analyzed. A decreasing of characteristic peak in chrysotile spectra related to increasing processing temperature was detected. The peak completely disappeared on samples processed at temperatures higher than 800 °C evidencing the complete transformation of chrysotile.



In conclusion the contemporary study of the same samples with all listed methods allows sure diagnosis on processed wastes.

References

Gualtieri A.F., Tartaglia A. (2000) Thermal decomposition of asbestos and recycling in traditional ceramics. Journal of the European Ceramic Society. 20 (9), 1409-1418.

AIRBORNE FIBRES IN ENVIRONMENTS WITH VINYL-ASBESTOS FLOORS: RISK ASSESSMENT AND PREVENTION CRITERIA

S. Peterle, D. Marcolina

Servizio Prevenzione Igiene e Sicurezza negli Ambienti di lavoro (S.P.I.S.A.L.) U.L.S.S. n.1 di Belluno, Italy

Nei decenni '60 – '80 gli edifici adibiti a scuole, ospedali, uffici, alloggi popolari hanno visto un largo impiego di mattonelle in resina di PVC, additivata con co-polimeri e pigmenti, contenenti percentuali variabili di amianto. Le fibre di amianto sono contenute in una matrice compatta, un materiale molto duro e resistente dal quale risulta improbabile un rilascio di fibre durante il normale utilizzo, se il materiale stesso è mantenuto in buone condizioni. In alcune situazioni di particolare sensibilità sociale, come gli edifici scolastici, nei quali la presenza di bambini e ragazzi, l'intensa sollecitazione dei pavimenti, la facile tendenza al deterioramento, ha creato un certo allarmismo dei cittadini, in particolare genitori e personale scolastico.

Negli ultimi tempi, inoltre, la possibilità di un riconoscimento di benefici previdenziali in base alla L.257/92 ha incentivato la richiesta, soprattutto tra il personale di pulizia e manutenzione di questi pavimenti, di conoscere il livello di rischio e quindi l'esposizione professionale a fibre di amianto negli edifici con tale materiale, soprattutto nei casi di degrado ed usura (vedi foto).

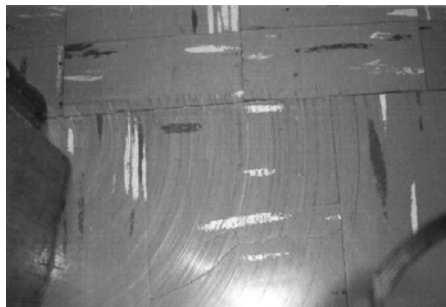


Foto – Piastrelle in vinil-amianto: rotture ed abrasioni superficiali possono liberare fibre?...

In assenza di sufficienti dati di letteratura sul livello di rischio derivante da tali materiali, il nostro Servizio SPISAL ha voluto effettuare la ricerca di fibre di amianto aerodisperse nei locali con pavimenti in vinilamianto nei principali edifici pubblici del nostro territorio, con particolare riguardo alle scuole. Lo scopo dello studio è di effettuare una corretta valutazione del rischio e fornire indicazioni per l'attuazione delle misure di sicurezza ed igiene necessarie.

La ricerca, avviata nel 1997, è stata completata nel corso del 2005, realizzando complessivamente:

- 1) n. 200 sopralluoghi preliminari con campionamento di pavimenti ed analisi del materiale;
- 2) n. 22 prelievi d'aria in locali con pavimenti contenenti percentuali diverse d'amianto, di diversa epoca e condizioni di usura (rotture, abrasioni superficiali), trattati a cera oppure no, con vario grado di sollecitazione meccanica, in relazione alla destinazione d'uso dei locali (aula scolastica, archivio, ecc.);
- 3) relazione tecnica finale ai datori di lavoro delle attività svolte nei locali, a ciascun Ente proprietario dell'immobile, e infine al personale di pulizia ed ordinaria manutenzione. La relazione conteneva sia l'esito degli accertamenti svolti, che le indicazioni sulle corrette procedure per la manutenzione ordinaria ed, eventualmente, per la bonifica definitiva.

Per i prelievi sono state utilizzati campionatori fissi (Zambelli e Tecora) ad un flusso di 20 litri al minuto, campionando un volume minimo di 4000 litri, filtri in esteri misti di cellulosa di porosità 0,8 micron e diametro 47 mm. Durante il campionamento, a centro ambiente (con finestre e porte chiuse), veniva mantenuto in funzione un ventilatore portatile in modo da creare un mescolamento dell'aria e una situazione di simulazione di "disturbo" creato dal normale utilizzo del locale in esame.

I campioni, sia di piastrelle che di fibre aerodisperse, sono state analizzate dal Centro Regionale di Riferimento per l'Amianto presso la Sezione Fisica Ambientale dell'ARPAV di Verona, con la tecnica di Microscopia Elettronica a Scansione (SEM) che, com'è noto, permette il sicuro riconoscimento della varietà di fibre di amianto.

Sono stati visitati 200 edifici (per la maggior parte scuole): in 88 di questi (pari al 44%) erano presenti mattonelle in vinil-amianto.

Sono state analizzate circa 120 campioni di pavimenti di diverso tipo ed età. Le mattonelle di lato 25 e 30 cm, rigide, a frattura netta, di vari colori e variegature, sono risultate composte da una mescola di resina vinilica e fibre di amianto (varietà crisotilo). Il tenore di amianto è risultato estremamente variabile: il contenuto medio nei diversi tipi di piastrelle rigide è del 12% (minimo 3% e massimo 45%); i pavimenti di più vecchia installazione (anni '60 e '70) presentano le percentuali più elevate (15-20%), mentre quelli posati alla fine degli anni '80 presentano percentuali molto più basse (3-5%). Esse sono caratterizzate anche da una facile tendenza al distacco per perdita di tenuta della colla, soprattutto in caso di infiltrazioni di umidità.

Al contrario, i pavimenti in rotolo (risalenti anche agli anni '60) ed i piastrelloni flessibili di lato 50 o 60 cm (utilizzati soprattutto negli ultimi due decenni), sono risultati esenti da amianto.

I risultati dell'indagine ambientale sulle fibre aerodisperse (22 filtri) hanno evidenziato un valore medio di 0,02 fibre/litro, molto inferiore al valore limite di riferimento (2 fibre/litro) previsto dalla normativa per determinare una situazione di inquinamento in atto. I limiti fiduciali superiori risultanti dall'elaborazione statistica secondo la metodica prevista dal DM 6/9/94, variano da 0 a 2,1 fibre/litro (media = 0,72; DS 0,48; range = 0,3-2,1; moda = 0,4). Non emergono differenze statisticamente significative tra le diverse condizioni prese in esame (piastrelle fessurate, tenore d'amianto, trattamento a cera, ecc)

La ricerca effettuata dimostra che la sola presenza di pavimenti con amianto, pur deteriorati, non rappresenta un rischio immediato per la salute degli occupanti, né ricorrono gli estremi per un riconoscimento professionale di esposizione a fibre cancerogene per il personale che abbia effettuato operazioni di ordinaria manutenzione (pulizia) di tali piastrelle o frequentato questi locali. Sono state tuttavia fornite indicazioni tecniche e cautele per evitare comunque esposizioni "indebite", ancorché occasionali, e precisamente:

A) Per gli Enti utilizzatori dell'edificio ("datori di lavoro"):

- segnalare immediatamente al proprietario dell'immobile le zone di degrado o rottura delle piastrelle in ciascun ufficio, evidenziate dai lavoratori;
- proteggere dall'effetto usurante delle sedie le zone sottostanti le scrivanie (ad esempio, con tappeti protettivi di facile pulizia e che non ostacolino il movimento delle sedie),
- prescrivere al personale di pulizia di applicare costantemente la cera protettiva e di evitare l'uso di spazzole abrasive, sia per la rimozione della cera che per la normale attività di pulizia; inoltre, di segnalare eventuali crepe o rotture rinvenute.

B) Per l'Ente proprietario dell'immobile:

- Attuare il programma di verifica periodica (sopralluogo e raccolta delle segnalazioni da parte degli Enti utilizzatori), e di manutenzione dei pavimenti, provvedendo immediatamente a sigillare eventuali fratture o soluzioni di continuità presenti, sia per limitare il più possibile un potenziale rischio di rilascio di fibre, che per poter garantire la sicurezza e l'igiene dei locali;
- Informare preliminarmente eventuali Ditte esterne (esempio: termoidraulici) della natura dei pavimenti in caso di necessità di interventi sull'edificio che possono disturbare, anche non intenzionalmente, i pavimenti in oggetto;
- In caso di futura necessità di bonifica, affidare il lavoro a Ditta specializzata, iscritta all'Albo Gestori Rifiuti (categoria 10 - Bonificatori di amianto).

C) Per il personale di pulizia (interno ed esterno):

- Effettuare la pulizia con panni umidi o spazzole morbide, frequente applicazione di cera, evitare l'uso di spazzole abrasive per la deceratura (scegliendo quindi cere che non richiedano tale trattamento); osservare e segnalare eventuali fessurazioni, rotture e distacchi delle piastrelle.

[1] E.P.A.: *Asbestos-containing Materials in Schools* – 40 CFR, Part 763 (1987);

[2] D. Marcolina, S. Peterle: *Risultati di un lavoro di rimozione dei pavimenti in vinil-amianto in una scuola elementare di Belluno. Atti del Convegno AIDII – Sezione Triveneto. Corvara*, 176, (1997);

[3] D. Romeo: *Pavimenti in linoleum con amianto: istruzioni per la bonifica. Ambiente & Sicurezza. Il Sole 24 Ore Pirola*; 20, 31-35 (2001);

[4] D. Romeo: *Pavimentazioni resilienti: la distinzione fondamentale tra linoleum e vinil-amianto. Ambiente & Sicurezza. Il Sole 24 Ore Pirola*; 22, 19-25 (2001);

[5] V.Verga, L. Gaburro: *Valutazione del rischio legato alla presenza e alla rimozione di pavimenti in vinil-amianto. Atti del Convegno AIDII – Sezione Triveneto. Corvara*, 167 (1997).

[6] S. Peterle, D. Marcolina, N. De Marzo, P. Curto, *Pavimenti in vinil-amianto: valutazione del rischio e modalità di bonifica, Atti del Convegno CNR*, 323-331 (2002).

HEALTH ENVIRONMENTAL ANALYSIS OF MATERIALS USED FOR A BEACH NOURISHMENT IN THE LIGURIA COAST

C. Bancomina⁽¹⁾, L. Bovone⁽¹⁾, G. Capano⁽¹⁾, S. Maggiolo⁽²⁾, A. Manti⁽¹⁾, S. Prandi⁽²⁾

(1) ASL4 Chiavarese, Department of Prevention.

(2) ARPAL, Genoa Department, Electron Microscopy Division.

Since coming into effect of the Law 257/92 the extraction of stony materials that contain asbestos was banned. Nevertheless the presence of ophiolitic (*green stones*) complexes in different Italian regions, with the potential risk due to the asbestos fibres release from rocky matrix, needs to be carefully monitored. The *green stones* are present in vast areas of Ligurian territory and they are used for building of railway ballast, hydraulic protection systems, as filling material and nourishment of beach. The handling control of such materials is rather problematic as doesn't exist a standardized method neither for sampling and preparation of the sample nor for a following analytical determination.

In a study carried out by ASL and ARPAL on the serpentine used for beach nourishment of Ligurian coast the method of sampling and analysis has been formulated and finalized to estimate a potential hazard of this natural material.

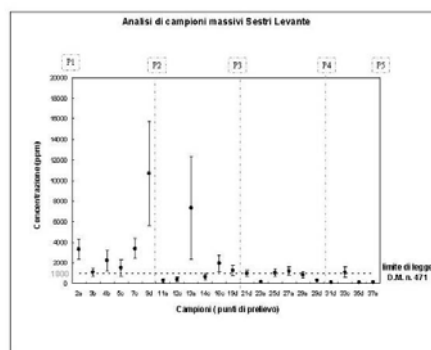
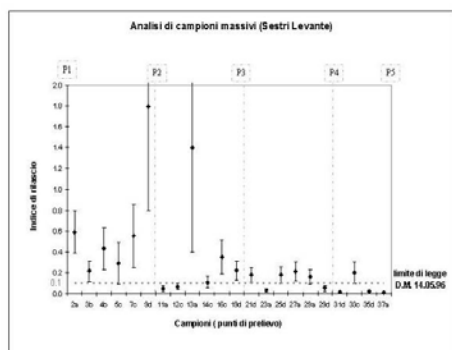
In our experience, the 45% of material was the serpentine got from excavation of motorway gallery, the 35% was obtained from dredging dry gravel river-bed and the 25% was originated from quarry of serpentine in a mountain hinterland. To select the drilling and sampling points, the recommendations of Decree of Ministry 471/99 have been followed, and the number of the samples to perform was decided in according to Decree 14/5/96. As was reasonable to suppose a ubiquitous distribution of pollutant, the site of sampling has been subdivided according to a grid of 38 areas,

each one 45 m on side. The more 22 significant areas has been located inside the grid and the random choice of the points of sampling inside each single quadrant has been done according to the "Statistical Methods for Environmental Pollution Monitoring" (R. O. Gilbert – Van Nostrand Reinhold Company 1987 NY USA). Inside each point of sampling a coring up to depth of 50 cm has been carried out and entire stratigraphy column has been mixed and homogenized appropriately.

A reference method for sample's preparation a reference method was suggested by Decree 14/5/96. The aliquots to test have been sieved through and the 5-50 mm fraction of granule for each sample was obtained. The relative density has been estimated for these fractions and 500 g of them have been closed in airtight metal cylinders to undergo the auto grinding process in order to simulate the damage caused by agents and by using the beach for playing.

For analysis has been used the method suggested by Decree 6/9/94. About 5 mg of dust coming from the auto grinding has been taken and then suspended in 200 ml of surfactant solution in bidistilled water. From this solution the volume of 4 ml has been taken and filtered on polycarbonate membrane. The filter obtained has been put forward for morphological and elemental analysis by SEM associated to EDS microprobe. The results obtained by identification of asbestos fibres and by measuring of their geometric dimensions (length and width) were calculated as value expressed in weight of asbestos on the filter, the concentration expressed as weight of free asbestos fibres and the value of Release Index. In the following evaluation of environmental and sanitary risks the reference values has been assumed the values of the Decree 471/99 (asbestos concentration <1000 ppm) and value of Decree 14/05/96 (Release Index < 0.1).

The graphs below evidence values, including the relative bar of errors, of 22 samples analyzed.



We can observe that for the major number of the samples from 2a to 19d (material from quarry) the law limits are over, while in the samples from 29d to 37a (sediment from dry gravel river-bed) the values are below the limits. The quantitative microscopic results are in accordance with preliminary macroscopic analysis of material and they have consented a characterization of the site with consequent request of security intervention in conformity with Decree 471/99 in the areas exceeding the limits.

The decontamination was realized by use of suitable covering material that has been preventively characterized. The choice of the covering thickness has been done on the basis of the analytical results obtained from the beach transversal profile evolution: the section between the foreshore line and 15 m above the coast was of 80 cm and the section over 15m and up to the wall of the promenade the coat was of 30 cm. The project of the environmental restoration approval has provided duty also to monitor the beach shore conditions yearly for the following five years by evaluation of the following parameters:

- the release index on the samples of sediment sampled up to depth of 30 cm;
- the environmental concentration of the airborne fibres;
- the evaluation of the beach profiles to verify the chronological progress.

It must be kept in mind that the possible reduction of 50% of the blanket utilized for security intervention could involve the restoration of the initial levels by inert material.

In conclusion, the work has got a way to define a standard procedure for quantity of asbestos presence evaluation in the suspected site, more than provide the analytical data to security body. In particular, the procedure indicated by Decree 14/05/96 is too much rough and doesn't supply indications of the major number of parameters indispensable for sample preparation as for example the velocity of rotation during auto grinding and analytical procedure for evaluation of relative density. On the analogy, the Decree 06/09/94 is not enough detailed about the indication on a way of counting of asbestos fibres and disregard the statistic evaluation of the minimum number of fibres. The limit value imposed by Decree 14/05/96 to allow the mining activity (I.R. < 0.1), is believed, it's more suitable to classify the waste to be put in the dump, rather than a material which after extraction frequently should be undergone to the further treatment of grinding and breaking. In this case the usage of material should be subordinated to the further quantifying of the asbestos fibres released in the successive stages of work.

THE OPHIOLITES, THEIR EXTRACTION AND THE ASBESTOS PROBLEM

O. Sala, F.Paoli, D.Menna

ARPA Sezione prov. Reggio Emilia

"Green stones" is a common term used for speaking about Ophiolites (igneous rocks rich of iron minerals). Ophiolites are inert matters very frequently used, in the present and in the past, in construction branch, for replenishment, like ornamental stones, etc. Green stones, however, can contain minerals with asbestos fibres, creating problems in public health that need scientific deepening.

Emilia-Romagna effectuated census of "green stones" pit in his area, to explain the division situation, the excavation modalities, and the stone uses.

Emilia-Romagna created an interdisciplinary task-force with technicians and delegates of the participating agencies, experts in health, environmental and excavation problems (Assessorato Regionale alla Sanità, Assessorato Regionale Difesa di Suolo e della Costa, Protezione Civile, ARPA Reggio Emilia, Province e Aziende USL di Parma, Modena, Piacenza e Reggio Emilia, Università di Bologna)

The group completed his work with the presentation of the book: "Le ofioliti, la loro escavazione, e il problema amianto". (<http://www.regione.emilia-romagna.it/amianto/pdf/pietreverdi.pdf>)

The book content can be summarized in:

- Mapping and geocoding of the 30 extracting sites localized in province of Modena, Reggio Emilia, Parma, Piacenza: 14 pits are exhaust and 16 are actives.

A specific research was conducted on the active pits to know geological and minerals peculiarities of Ophiolites extracted, the excavation modalities, the workers number and the destination of the extracted materials. Low D.M. 101 (18/02/2003) requires mapping and geocoding; this data are contained in final results of "Progetto Mappatura Amianto" that Region Emilia-Romagna has committed to ARPA Reggio Emilia.(Fig.1)

- Results of analysis on extracted material in different pits, in order to evaluate the presence and the realising measure of absesto fibres, referring to the actual scientific methods provided for law
- Results of environmental samples in tips and on workers involved
- Results of epidemiology investigation obtained from Emilia-Romagna Mesoteliomi register (updated to march 2004), of Istituto Superiore della Sanità and of AMOS project of CNR (Life Project 99/NU/IT/000153)

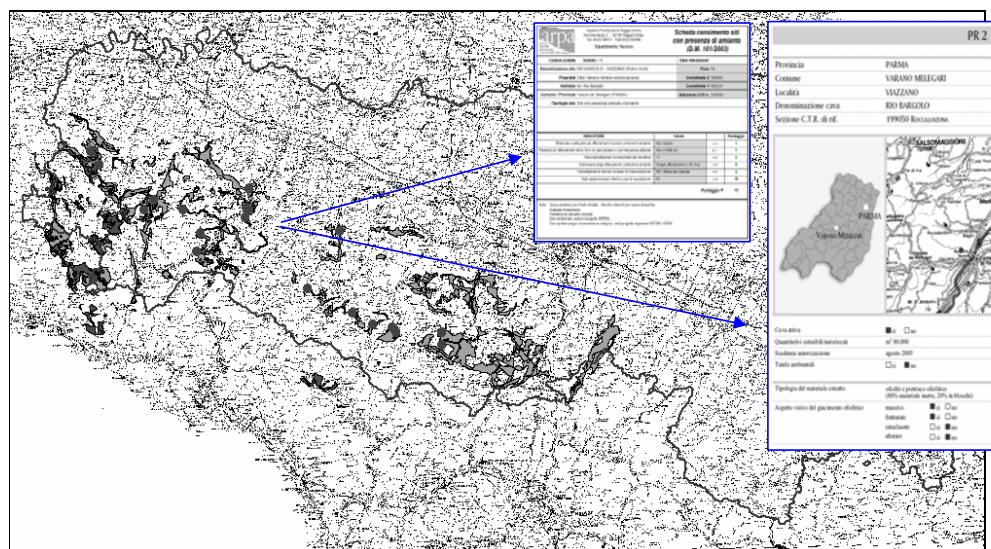


Fig.1: mapping and geocoding pits in Emilia-Romagna

Considerations about environmental data

The pollution levels due to asbestos fibres, detected by this and other research (AUSL Toscana, project ISPEL – AUSL Parma), result lower than exposure limit (0,6 or 0,2 ff/cc), but important regarding indicated value under D.Lgs 277/91 (0,1 ff/cc).

Environmental data result, in the main, indicative for risk reduction prevention actions.

The first pollution cause is detected in dust dispersion: the excavate materials handling, means of transport movements and the mill working, which is the most critical phase.

It was very difficult and laborious to characterize Serpentine in materials and in air.

It is very difficult to count the fibres dispelled in air, for environmental risk and for workers risk evaluation, due to the presence of fibrous object (es. Prisms) not discernible by fibres, especially with small particles (es. $D < 1 \mu\text{m}$) (Fig. 2 and Fig. 3).

The SEM observations highlighted this problem.

The literature relates analysis data obtained by TEM (Transmission Electron Microscopy). This technique could be very useful to characterize chrysotile – lizardite – antigorite, but it is very expensive, so difficulty applicable in periodic atmosphere analysis.

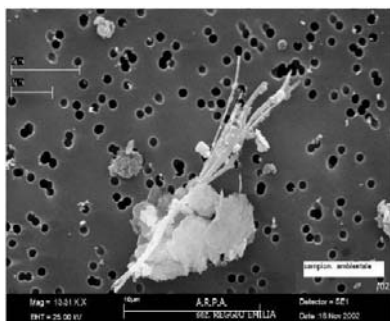


Fig.2: fibres

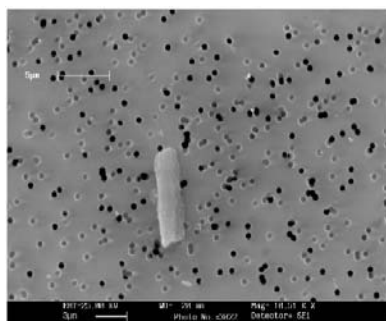


Fig.3: prism

TRAINING AND INFORMATION: CONSCIOUSNESS AND COMMUNICATION ON THE ASBESTOS TOPIC

Alberto Verardo

Regione Liguria Servizio Prevenzione

Il tema delle bonifiche da amianto offre innumerevoli spunti di approfondimento per chiunque debba o abbia necessità di confrontarsi con essa.

Uno di questi, di rilievo non secondario sia per coloro che detengono che per coloro che bonificano, è riconducibile al ruolo ed alle finalità di una corretta informazione in materia ed all'importanza di una idonea formazione per chi manipola manufatti contenenti amianto.

Negli incontri di introduzione ai diversi corsi per operatori delle bonifiche da amianto che le singole Amministrazioni Provinciali della Liguria svolgono a favore delle imprese che attuano o intendono attuare bonifiche da amianto presso i Centri di formazione professionale gestiti direttamente o con esse convenzionati, o in ogni altra occasione di approfondimento promossa da soggetti pubblici e privati, la Regione porta un contributo preliminare che ha lo scopo di inquadrare la problematica correlata all'asbesto e, laddove viene attuata, l'attività formativa, nel contesto del Piano Regionale Amianto.

L'illustrazione dell'argomento trae origine dalla visione di un dipinto realizzato da William Hogarth denominato "Falsa prospettiva" osservando il quale è possibile evidenziare – per poi derivare da questa evidenza gli ulteriori elementi di interesse – l'importanza dell'attenzione al reale contenuto delle cose che a volte non viene adeguatamente compreso.

Causa di ciò è frequentemente un esame superficiale o sommario dei fatti e delle circostanze, conseguenza di atteggiamenti personali di scarsa attenzione dovuta alla convinzione di possedere già completa ed esaustiva conoscenza del necessario, peccando di poca umiltà e di ridotta capacità a mettersi in discussione.

Da questa premessa stimolante, dovrebbe potersene derivare la necessità di crescita in consapevolezza per assicurare lo svolgimento di reali e concrete azioni integrate di prevenzione, connesse alla conoscenza ed alla comunicazione in tema di amianto, finalizzate alla promozione ed alla protezione della salute e dell'ambiente.

La situazione ambientale esistente, caratterizzata da un reale e diversificato livello di inquinamento da fibre di amianto, deve far sempre e comunque riflettere sull'importanza della valutazione del rischio e degli effetti dei determinanti ambientali sulla salute umana ed anche sul ruolo che hanno e sempre più dovranno avere gli organismi responsabili della protezione della salute e dell'ambiente.

In modo sempre più marcato deve essere presa consapevolezza della necessità di incidere su questa situazione attraverso la costruzione di un sistema che sia capace di sostenere le molteplici azioni che si intraprendono ed al tempo

stesso possieda quella flessibilità necessaria ad essere in grado di adattarsi con tempestività alle modificazioni che intervengono in materia.

Mutamenti che il tempo ha insegnato ad attendere a volte molto, altre volte meno, sempre con rispetto ed attenzione perché frutto delle conoscenze scientifiche in costante evoluzione e della altrettanto sistematica ricerca di migliore corrispondenza ai fini di tutela.

La conoscenza e la comunicazione in tema di amianto intese come sistema che si colloca all'interno della nostra quotidianità e si rapporta con la nostra realtà di vita.

L'importanza dunque dell'informare, per consentire una efficace azione di prevenzione attraverso la reale conoscenza, ma più ancora dell'imparare a comunicare, per trasmettere consapevolezza.

L'importanza del formare per contribuire a circoscrivere l'inquinamento con azioni che non apportino ulteriori occasioni di incremento ed a tutelare la salute nella consapevolezza che ciò è possibile ed è un dovere per chi si confronta con la problematica amianto.

Per comunicare e per formare in tema di amianto molti possono essere i modelli cui riferirsi o ai quali ispirarsi, ma chi con essi si confronta o si cimenta, deve sempre avere presente il più reale e concreto punto di partenza possibile: il bisogno di chi chiede o di chi attende riscontro; deve altresì avere, quale obiettivo da raggiungere, la consapevolezza della problematica con la quale si confronta, attraverso la comprensione della stessa.

Contents

Opening Session

L. Kazan-Allen	Global impact of Asbestos	3
J. Cherrie	Exposure limits in different countries	3
S. Clarelli	How to work with asbestos safety	4
F. Damiani	Italian Asbestos laws	5
M. Alessi	Italian National Asbestos Commission and its workgroups	6

Session: Analysis in air

A. D. Jones	Current issues in asbestos fibre counting: changes in rules and national and international comparability	11
B. Tylee	The MDHS87 method and strategy for the discrimination of airborne fibres in the UK	11
G. Zanetti	Simplified analytical methods for a hard-mapping of asbestos in civil buildings	12
S. Massera	PCOM determination of airborne asbestos fibres: inter-laboratory comparison and validation proposal for an analytical method	14
M. Bruzzone	Multi-year experience: a plan for the improvement of the analytical quality of 15 ligurian laboratories for the measurements of the concentration of the asbestos fibres in air (PCOM)	16
H. Kropiunik	Phase contrast microscopy versus scanning electron microscopy: critical discussion of asbestos monitoring methods based on empirical data from the Vienna international centre	17
A. Somigliana	Uncertainty assessment during PCOM filters observation	18
R. Stanescu	Physico-chemical methods to identify asbestos in occupational environment	20
E. Lauria	The necessity of SEM analysis in outdoor environment monitoring of airborne asbestos fibres	22
M. Bergamini	Monitoring of airborne fibres during remediation of the abandoned asbestos mines of Balangero and Corio	24
A. Cattaneo	Dimensional microscopic analysis of asbestos bundles released in atmosphere from an asbestos cement roof	26
G. Cecchetti	Specific analytical techniques for asbestos analysis in air: comparison and evaluation	27

Session: Analysis in soils and bulk materials

B. Tylee	Quality of analyses of asbestos in soil	31
P. Di Pietro	A new method for the measurements of low fibre levels in soils with XRD and FTIR	31
S. Shuttler	Sampling materials and fibre identification by polarised light optical microscopy (HSE test method MDHS77)	32
E. Lauria	Methodological approach to the analysis of asbestos in rocks	32
C. Cazzola	Methods and applications for quantitative analysis of asbestos in rocks and soils by light optical microscopy	34
C. Groppo	Quantitative analysis of fibrous minerals in rock samples using BSE images and micro-raman spectroscopy	36
C. Rinaudo	Raman spectroscopy: a rapid technique to identify asbestos phases	37

Session: Analysis in liquids

S. Malinconico	International and Italian regulations concerning asbestos limits in liquids	41
A. Brancia	Determination of asbestos in water by FT-IR technique: a proposal for an analytical routine-model	42
O.Sala	Investigations on the occurrence of asbestos fibers in drinking water	43
L. Zamengo	Analysis of asbestos fibres in hazardous waste landfill leachate: the FALL project	45

Session: Exposure monitoring and regional mapping

D. Bard	Personal passive samplers use to monitor the exposure of maintenance workers (industrial plumbers) to asbestos	49
S. Clarelli	The choice of individual protection devices for asbestos remediation workers	49
T. Marchi	Professional exposure and environmental pollution during remediation of asbestos-containing materials	50
M. Guidi	Asbestos remediation in acetylene cylinders	52
A. Verardo	Informatic system for data analysis and evaluation	52
L. Amato	Evaluation of the asbestos risk in the alta val Lemme area (Piemonte)	53
G. Bultrini	Microscopic and microchemical investigations on the fibrous amphiboles from Etna volcano district (Catania-Italy)	55
A. Gianfagna	Fibrous and asbestos-like minerals in volcanic soils of Biancavilla (Catania): identification, classification and environmental impact assessment	56
E. Renna	Asbestos containing material mapping of Emilia- Romagna region: application of 18 D.M. 101/2003	58
B. Sperduto	Environmental pollution from airborne asbestiform fibres: Development of fibre propagation maps	60
L. Fiumi	Mapping of the asbestos-cement by remote sensing and GIS	62

Session: Indirect biological methods

S. Capella	Indirect monitoring of asbestos by mineralogical investigations of sentinel animals lungs	67
M. Tomatis	Asbestos fibres in human urine reflecting environmental exposure measured by long and short term air monitoring in the lanzo and susa valleys	67
T. Battaglia	Monitoring of respirable mineral fibres in the biancavilla area (sicily) by sem-ed analysis of urine	68
E. Fornero	A cattle model of environmental exposure to asbestos in lanzo and susa valleys (piedmont region): possible fibre accumulation mechanism in cow lungs	69
D. Bellis	Mineralogical investigation of human biological material to detect the presence of breathable mineral fibres in airborne dust	70

Poster session

P. Avino	Fibrous material characterization in an urban area at high density of autovehicular traffic	73
A. Baj	Control of airborne fibres by scanning electron microscopy (SEM) and phase-contrast microscopy (MOCF) during asbestos removal	74
L. Bologna	Problems concerned with the natural presence of asbestos	75
V. Cardile	Involvement of oxidative stress and cyclooxygenase in the effects induced by the asbestos-like fluoro-edenite fibres	77
P. Di Pietro	Determination of asbestos in vinyl floor tiles by FT-IR technique	79
C. Fanizza	Polycrystalline fibre size distribution by SEM	79
L. Groppo	Quantitative analysis of chrysotile in antigorite-serpentinites using spectroscopic and thermal analysis	81
A. Gualtieri	Long-term asbestos monitoring in life and professional environments of selected Italian sites	81
P. Marescotti	Naturally occurring asbestos minerals from metaophiolites: rationales for custom-designed analytical constraints	83
S. Massera	Asbestos substitutive materials: analytical protocols for classification of man-made vitreous fibres as carcinogenic agents	85
G. Pecchini	Analytical evaluation of wastes containing asbestos after inertization treatment by pyrolytic process	87
S. Peterle	Airborne fibres in environments with vinyl-asbestos floors: risk assessment and prevention criteria	89
S. Prandi	Health environmental analysis of materials used for a beach nourishment in the Liguria coast	90
O. Sala	The Ophiolites: their extraction and the asbestos problem	92
A. Verardo	Training and information: consciousness and communication on the asbestos topic	93