Project "Size Selective Personal Air Sampling Using Porous Plastic Foams"
(PoFAS)
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Final Project Report
(Condensed Version)

Porous Foam Aerosol Sampling
(PoFAS)

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Nomenclature

A	slope factor in g/%
A/N_C	weight change in g per cell per % of change of humidity
C_a	concentration of ambient aerosol
C_s	concentration of sampled aerosol
d_{ae}	aerodynamic diameter
d_{cell}	cell diameter
d_{50}, D_{50}, D50	particle diameter for which the penetration is 50 %
d_f	diameter of foam filament
E_s	sampler efficiency
FID	flame ionisation detector
g	acceleration due to gravity
GC-MS	gas chromatography-mass spectrometry
LOD	limit of detection
LOQ	limit of quantitation
M	mass of a foam at relative humidity rh, $M = A \cdot rh + M_0$
M_0	dry mass (rh = 0 %) in g
N_b	number of blanks
N_C	number of cells in the volume of the whole plug, $N_C = V_{plug} / V_{cell}$
Ng	gravitational parameter
P	particle penetration
po	porosity / ppi
rh	relative humidity in %
St	Stokes' number (inertial parameter)
U	velocity of air (e.g. through a foam)
V_{plug}	volume of foam plug
V_{cell}	volume of foam cell
W	wind velocity
γ	density of air
η	viscosity of air
σ^2	uncorrectable variance associated with each mass difference measurement
σ_w	standard deviation in collected mass determination, $\sigma_w^2 = \sigma^2 (1 + 1/N_b)$

1 Project participants

The project was carried out by the contractors:

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2 Abstract

The inhalation of dust at work remains, in the 21st century, one of the most important causes of ill-health related to work. In the industrialised nations several million workers (including retired workers) have been killed or injured by dust at work. In order to get reliable data of worker's exposure, a measurement system ideally needs to be able to determine the three particle size fractions according the standard EN 481 'Workplace atmospheres: Size fraction definitions for measurement of airborne particles' (CEN, 1993).

A new reference method for the simultaneous measurement of hazardous particulate matter according EN 481 was developed. This development includes the design and testing of two three stage personal air samplers based on the existing IOM and GSP samplers for the inhalable fraction incorporating additional porous plastic foams. Two foam plugs with different porosity are used to select the thoracic and respirable dust fraction, which reach the lower parts of the lung.

Polyurethane foam has been found to serve well as a sampling and selection medium for particles. The physical and chemical behaviour of porous foams was investigated using microscopy (optical, SEM), elemental and organic chemical analyses. A semi-empirical model was developed and used to predict the particle penetration and foam plug geometries, suitable as good starting points for particle penetration tests using polydisperse dusts (glass microspheres) in wind tunnel (velocity: 0.15 m/s) and calm air chamber tests. The results indicate that selected foams with predicted geometry and porosity comply with the required penetration curves sufficiently well.

Besides the development of a sampler, special attention has been paid to the development of suitable analysis procedures to determine the mass and chemical composition of the sampled dust collected in each stage.

Prototype samplers have been constructed and field tests gave information on the handling. By appropriate choice of foam selection characteristics, a sampler of this type can collect the

respirable fraction on the filter, the thoracic fraction on the filter plus the adjacent foam plug and the inhalable fraction on the filter plus both plugs. Recommendations for a later use in different national air sampling systems shall be given in order to reach a higher degree of European harmonisation in occupational exposure measurement.

3 Introduction

Occupational diseases of the respiratory tracts like pneumoconiosis and others related to the influence of airborne substances play a major role in the compensation by occupational insurances in all member states of the European Union. In order to get reliable data of worker's exposure, a reliable measurement system is indispensable. Procedures for the measurement of chemical agents have to fulfil the general requirements of the EN 482 (“Workplace atmospheres: General requirements for the performance of procedures for the measurement of chemical agents“) and the EN 689 (“Workplace atmospheres: Guidance for the assessment of exposure by inhalation to chemical agents for comparison with limit values and measurement strategy“). The purpose of a personal dust sampler worn by a worker is to estimate as accurately as possible his/her occupational exposure to the aerosols in the workplace environment. Ideally, such a personal air sampler should collect the same aerosol size fraction at the same concentration as that inhaled by the worker.

The decision as to which dust fraction should be collected in a given workplace depends on the potential health effects relevant to that particular situation. According the general recognition that all particles capable of being taken into the body during breathing could present either a specific or a non-specific risk to health, three particle fractions have been defined. They are stated in a European standard, the EN 481, which is in conformity with international standards from ISO (International Standards Organisation) or recommendations from the ACGIH (American Conference of Governmental Industrial Hygienists). The resulting definitions of inhalable, thoracic, and respirable dust fractions relate to the regions of the respiratory tract to which that dust can ultimately penetrate and cause health effects.

A new generation of sampling instrumentation is now required to match these criteria, A wide range of different personal air samplers is employed in occupational hygiene practice. However, these are based largely on the old conventions for total and respirable dust which are no longer valid. They are also able only to sample one dust fraction. In order to get precise data of the workplace exposure, these three dust fractions must be sampled simultaneously at the working person itself.

This EU project POROUS FOAM AEROSOL SAMPLING (contract SMT4 CT96 2137) dealt with the development of a method for a simultaneous sampling of these three dust fractions and applicable analysis methods. The development resulted in a simple, easy to handle sampling technique, which shall be adapted to different existing national sampling systems in order to get a recommended sampling procedure for European wide use in occupational hygiene. Exposure data coming from this sampling method will serve to provide a precise and comprehensive picture of occupational exposure. This is a necessary requirement for an occupational exposure assessment as part of a risk assessment for priority substances according the EC Existing Substances Regulation (93/793/EEC) (ESR).

A survey of published literature in this field revealed that the only porous material whose aerosol penetration characteristics has been studied extensively is polyurethane foam (PUF). PUF is in widespread use as an aerosol filtration medium for air cleaning and its filtration properties have been extensively studied (Brown, 1993). Experimental data describing the aerosol penetration as a function of foam porosity, thickness and face velocity are presented by Gibson and Vincent (1981) and Wake and Brown (1991). These data indicate that the aerosol penetration properties are dominated by inertial capture of particles at high face velocities, and gravitational sedimentation at low face velocities. Owing to its very open structure, the capture of particles by diffusion is not thought to be significant under the conditions most relevant to personal aerosol sampling (Vincent et al.,1993).

For this material an empirical model for aerosol penetration has been developed and already applied to the design of aerosol samplers. Although the model is limited in some important aspects and does not entirely cover the range of conditions required for personal aerosol sampler design, it has nevertheless been shown to provide a very good starting point for further study. Experimental validations of the model indicate that it is able to predict the particle aerodynamic diameters at which 50% aerosol penetration occurs to within 30% of the true value, even for foam plugs with specifications outside the original range of application of the model.

3.1 Analysis methods

The analytical purity is generally good. PUF has already been used as a sampling medium for a wide range of organic and inorganic pollutants and a variety of methods developed for recovery of the sampled materials from the foam matrix.
Metals of toxicological interests for humans may be analysed in foam materials by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) or Atomic Absorption Spectroscopy (AAS). ICP-MS analysis of metallic compounds collected on foams has been carried out by HSL and IOM. The X-Ray analysis of CIP10 foams loaded with quartz dust is described in detail by the French standard NF X43-295 (1995) - Determination par rayons X de la concentration du depot alveolaire de silice cristalline - Echantillonnage par dispositif a coupelle rotative. HSL have used X-ray fluorescence to directly analyse inorganic contaminants on thin PUF plugs. There is also an extensive literature on the analysis of complex organic substances collected on foams.
For the analysis of organic compounds thorough cleaning of the foams before sampling is important and sample preparations include extractions by organic solvents in Soxhlet cartridges, supercritical fluid extraction with carbon dioxide or modified CO_2 and cryocondensation. Associated fractionation steps depend on the levels of analytes present and the complexity of mixtures and may be time-consuming. Organic chemicals have been determined principally by separation techniques such as gas- or high-pressure liquid chromatography, with detection and identification by mass spectrometry.

3.2 Weighing of foams

The weight stability of PUF has generally been found to be poor in all but the most rigidly controlled environments, but systematic changes due to moisture uptake can be addressed by the use of blanks such that a ‘tare’ weight is used to correct for the weight changes. Therefore

the variability of the weight changes rather than their magnitude limits the precision of gravimetric analyses. This problem has been explored by both INRS and by HSL.
These studies indicate that pre-treatment of PUFs by washing improves their weight stability and hence the precision of gravimetric analyses. Furthermore, mean weight changes are lower for smaller PUF plugs having lower tare weights, and can be minimised by careful environmental control in the conditioning and weighing environment.

This EC research project should concentrate on PUF as this material is cheap, easily obtainable, most well characterised and has a track record of successful use in aerosol sampling. Before experimental measurements of foam were carried out, it was essential to contact suppliers of PUF in order to investigate the availability of differing foam porosities, and the potential for a higher degree of analytical purity and quality control by the manufacturer. The assessment of foam quality comprised physical and chemical characteristics. The cell diameter was found to be the main characteristic. The experimental work needed to be carefully planned to cover the range of foam porosities, dimensions and flow rates most likely to be relevant to the use of PUF in personal aerosol samplers. After predicting foam plug porosities and geometries with help of a theoretical model several tests for particle penetration through foam plugs with nominal porosities between 45 and 170 pores per inch (ppi), equal to 1.5 and about 0.25 mm cell diameter, were carried out. The resulting penetration values were compared with the model. On this basis a few sets of plug geometries for the two size selective foam plugs were chosen to fit into the IOM and GSP inhalable samplers. Penetration tests had to show the applicability. Prototype samplers were constructed and tested in laboratory and field trials.

Besides the hardware of a sampler, special attention was paid to the development of suitable analysis procedures to determine the mass of the sampled dust of each stage and its chemical composition, since they will be different to existing procedures. Adapted methods for nickel and lead dusts were under development.

4 Quality of foam materials

Since foam material is industrially produced in large quantities, there will be differences in the grade of porosity and its constancy. Suitable measurement methods have to be either applied or developed to determine its porosity and the analytical purity. Other points to be considered were the preparation of the foam material in order to support the experiments with clean and homogenous plugs. The procedures for cleaning the foam, e.g. washing and using different solvents, and for coating with suitable substances were to be developed.

4.1 Determination of porosity

Three simple techniques can be used to determine the porosity by optical means: (a) visual counting of the number of cells from images taken with a camera and microscope, (b) measurement of cell diameter, (c) measurement of thickness of the pore filament. The procedure (b) seems to be most appropriate and the cell diameter parameter is useful in the theoretical model.

Reticulated polyurethane foams (PUF) were selected for the project, which are characterised by a three-dimensional skeletal structure with few or no membranes between strands. PUF is a flexible material, regains its form after physical impact, is widely used and produced and therefore available in diverse porosities and cheap in application. PUF is also quite stable under atmospheric conditions and resistant to some chemicals. These polymers can be prepared to have reactive hydroxyl groups and be used as a polyol in the preparation of polyurethane foam. Through special thermal reticulation techniques, it is possible to produce flexible skeletal foam structures without cell membranes ("open-pore" foam). In this process, most cell walls are ruptured to varying extent. The breaking of membranes within the cell structure permits flow of air or liquids through the foam material. A common technique for cell opening (reticulation) consists of creating vacuum around the foam in a heated autoclave, filling with hydrogen gas and igniting an explosion.

To characterise the foam porosity, the manufacturers use the notation of ppi, the number of pores per (linear) inch, a unit for expressing pores count of a foam. In practice, the criteria may be questionable in terms of comparability between similarly specified products. The values of ppi for a product are only given in steps of 5 ppi, which is probably not precise enough for predictions of particle penetration.

The three dimensional structure of PUF is observed by optical microscopy (Fig. 1). It appears that the unit cell is polyhedrical.

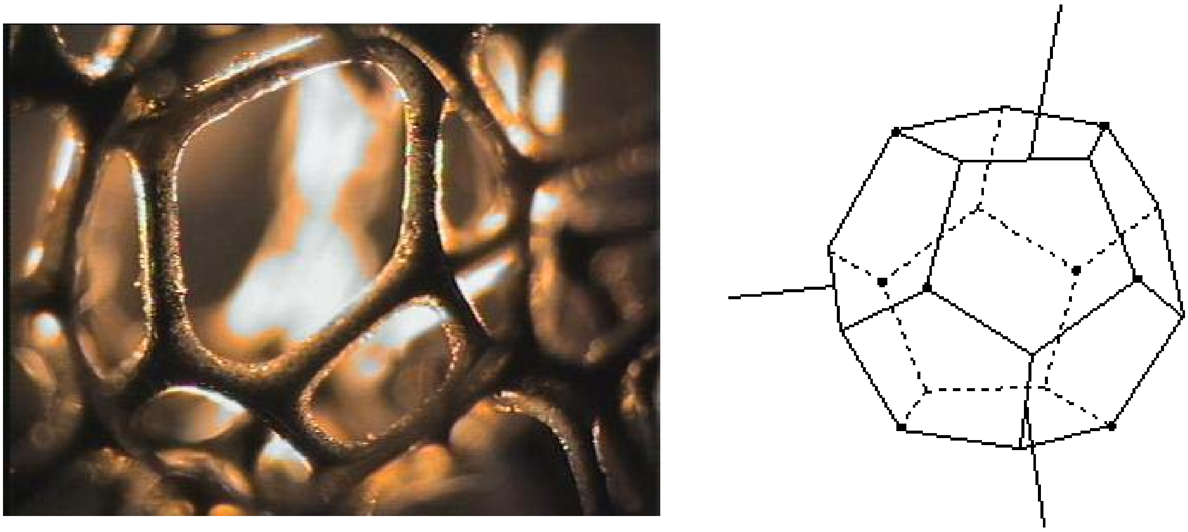

Fig. 1: Cell in foam matrix in form of a dodecahedron

A pore is understood as the smaller hole in the wall of a cell. The results show smaller deviations when measuring the number of pores per length rather than the pore diameters. The pore diameter is too variable, as can be seen in Fig. 1.

Assuming the three dimensional cells are dodecahedron shaped (12 fold a pentagon in shape of a football), the determination of cell diameters may be a good characterisation of the porosity. The cell in the primary shape is the closed bubble and after reticulation it ideally represents the dodecahedron structure with residual filaments at the edges. The cell diameter represents the mean value of the inner diameter (Fig. 1). In practice such ideal cells are to be found on the cut surface of the foam. Those are selected for determination of the diameter which are cut in the middle. The diameter can be calculated with help of scales in the microscope or on pictures. This method is also used by the manufacturer Recticel (Recticel 1994) and is more precise than counting pores per length or pore diameters. An empirical relationship exists between the ppi-value (pores per inch) and the cell diameter. The manufacturer should be able to produce and select foam material batches according to this measure, so that errors in ordering the correct porosity should be minimised.

A set of data determining the cell diameters of foams with different porosity using optical stereo microscopy revealed a total accuracy ranging from 7.3 to 13.8 %, the higher values at smaller cell diameters. This total accuracy is composed by a systematic error on how precisely to determine a distance on a scale of a microscope and the random error occurring in a series of diameter values. The systematic error is almost smaller than the random error.

The third measure to determine the porosity is thought to be the filament diameter d_f. It can be measured by use of an optical microscope with high magnification (approximately 40 x) or in scanning electron microscopes. Aitken et al. (1993) proposed a relationship for the porosity $Po = f\,(1/d_f)$. The determination of the filament diameter also was characterised with larger variations than measuring the cell diameter.

The fourth measure for the determination of the porosity was the pressure drop of air flow through a foam. The parameters are air flow per surface area and the thickness of the foam plug. The resulting pressure drops are in the range of a few Pa for foams with geometries of interest. Since measurement errors are also in the range of one or two Pa, this method to determine the foam porosity is at the limit of detection and therefore not very suitable. Especially for foams with low porosity, i.e. large cell diameters, it will be not of much use. For foams with small cell diameters this could be a way to determine or control the porosity. In comparison to the direct measurement of the cell diameter, no advantage is seen in pressure drop measurements.

4.2 Particulate and inorganic impurities

Particulate contamination can arise from cutting, transportation and during storage of foams. The washing method with detergents described by INRS was used to wash the foams (NF X 43-295, 1995). The particulate impurities after washing with water and detergents are measured as the loss of weight by the foam expressed in weight-%. The result of 8 replicate washings of PUF disks (about 200 mg each) gives a mean value of 1.38 % loss of weight assimilated to particulate impurities present in the foam (Table 1).

Table 1. Removal of particulate impurities from two selected PU foams by water + detergent solutions.

Foam type	Weight before treatment [mg]	Weight after treatment [mg]	Loss of weight [mg]	Loss of weight [%]
45 PPI #1	210.055	207.202	2.853	1.36
45 PPI #2	209.559	206.597	2.962	1.41
45 PPI #3	213.598	210.753	2.845	1.33
60 PPI #1	261.599	257.972	3.627	1.39
60 PPI #2	259.837	255.926	3.911	1.51
60 PPI #3	259.998	256.654	3.344	1.29
60 PPI #4	262.095	258.532	3.563	1.36
60 PPI #5	263.884	260.234	3.650	1.38
		Mean value of loss of weight in [%]		***1.38***

[a] Mean standard deviation on the weight is here ± 0.050 mg.

Individual weight losses may be significant because the operation itself (drying the foam for 5 hours at 120°C in a ventilated oven) may also contribute for around 0.4 %. As a matter of fact, the amount of weight loss depends on the initial state of the foam material, the handling and the operations.

Determinations of trace metals in the base PUF materials were performed by atomic absorption spectroscopy focusing on metals. The analysis method at IST for foam digestion (1 gram of PUF) used concentrated nitric acid in a Teflon autoclave at 120°C and appeared to give a suspension of black particles. After filtration or centrifugation a clear solution was gathered for analysis. The ICP-MS method at BIA used an acid dissolution consisting of 25 % HCl, 65 % HNO_3, 1+2 parts, with reflux cooking for 2 hours. Again residue black particles from the foam matrix had to be filtered. The analysis of washed blank foam material revealed especially impurities of tin, magnesium and calcium. All other elements could not be detected.

(60 ppi, 2 production batches from Foam Engineers, UK, originating from Recticel, 6+5 specimens)

elemental content in µg/g foam	IOM batch 60 ppi	HSL batch 60 ppi
Tin (Sn)	43 µg/g foam	5.6
Magnesium (Mg)	5.4	11
Calcium (Ca)	27 (not washed before) <25 else	<25

(10, 80 ppi, from Nauer, CH, Recticel Bulpren, 470 and 1625 µm cell diameter)

elemental content in µg/g foam	Nauer 10 ppi	Nauer 80 ppi	Recticel Bulpren d_{cell} = 470 µm	Recticel Bulpren d_{cell} = 1625 µm
Tin (Sn)	200 µg/g foam	< 25	60	< 25
Magnesium (Mg)	< 25	65	< 25	30
Calcium (Ca)	appr. 500	appr. 500	appr. 520	appr. 320

	± appr. 20 %	± appr. 20 %	± appr. 20 %	± appr. 20 %
Nickel (Ni)	< 25	< 25	< 25	< 25
Lead (Pb)	< 25	< 25	< 25	< 25

4.3 Identification of organic impurities

Some classes of products were anticipated. These included anti-oxidants (materials which improve the resistance of the foam to oxidative type reactions when added to a flexible PUF formulation, such as scorch [discoloration in centre of foam buns]); plasticisers (chemical additives in a flexible PUF formulation that generally serve to increase the flexibility of the foam structure); fire retardants; silicon surfactant (organosilicon compounds that exhibit surface active properties, add stability to the liquid foaming mixture so that collapse of bubbles is retarded and flow ability is increased) and catalysts (a chemical that changes the rate of reaction of the chemical process, but is not consumed or produced during the reaction). The major compounds found in PUF are reported in Table 2.

The identification of the peaks was realised by gas chromatography-mass spectrometry (GC-MS). The mass spectra of peaks were compared to those of standards. Several solvents were used to extract the organic matter present in the foam disks. The general profiles of the FID-gas chromatograms for each of the solvents are similar, the differences come from the amount extracted for a particular compound due to affinity for the respective solvent. Peaks A and B could not yet be definitely assigned an identity and amounts are calculated relatively to identified peaks. These quantified compounds represent 95% of peaks detected by GC-MS. Other identified minor peaks in are:
2,4 TDI, Diisobutyl phthalate, Dibutyl phthalate, Hexadecanoic acid, Diisooctyl phthalate, Benzyl octyl phosphate, Terbutylphenyl diphenyl phosphate.
The concentrations of these compounds are below than 0.02 mg/g of foam.

Table 2. Loss of weight after ultrasonic extraction of polyurethane foams. Quantification of identified peaks by GC-MS. Three solvents were used ranked in order of polarity.

Compound name		Concentration: mg/g foam	
Solvent →	HEXANE	ACETONE	METHANOL
Mass of treated foam →	1005mg	1023mg	967mg
Peak A	3.77	2.85	2.50
Benzyl butyl phthalate	0.08	0.05	0.05
Triphenyl phosphate	0.09	0.07	0.07
(2-ethylhexyl) diphenyl phosphate	3.43	2.25	2.05
Di(2-ethylhexyl) phenyl phosphate ?	0.35	0.19	0.15
Squalene	0.05	0.04	0.04
Peak B	1.39	2.57	2.07
total	9.16	8.02	6.93

5 Modelling particle penetration through foams

The design model should enable the user to calculate dimensions and foam specifications for a desired particle size-selective behaviour at a chosen flow rate. A large series of experimental measurements of aerosol penetration through polyurethane foam provided the raw data for developing the design model. Aerosol penetration measurements were carried out in three laboratories, HSL, IOM and INRS. HSL and IOM repeated tests on the same selection of foams, whereas INRS tested only a subset of the foams. The foams for testing were taken from the same manufacturing batches. The method for testing at HSL is described fully by Kenny and Stancliffe (1998). Tests at the other laboratories were carried out using very similar methods, and the same test aerosol, however different versions of the Aerodynamic Particle Sizer APS (TSI Inc.) were used in each case. The main point of interest for the sampling applications under consideration is the reliability of the data around 4 µm and 10 µm, since these are the d_{50} values for which our foam modules will be designed. In these ranges the differences between the INRS and HSL results are too small to be of concern in the development of the design model, particularly in the light of uncertainties in determination of the foam porosity. Hence it is justified to pool the HSL and INRS data.

The Vincent *et al.* (1993) semi-empirical model for foam penetration is based upon classic filtration theory for depth filters, and takes into account both sedimentation and inertial modes for aerosol deposition within the foams. Since the Vincent model appears to be a good starting point for foam module design it is worthwhile to re-formulate it in order to correct it's minor faults. The first point to consider is the substitution of the empirical parameter, 'fibre' diameter, with a traceable measurement of foam porosity. Contacts made with the foam manufacturer (Recticel International Development Centre), revealed that although vendors of porous foam continue to classify foam grades according to the parameter 'pores per inch (ppi)', the manufacturer now checks the foam grade by measuring the cell diameter in µm. Recticel have developed an in-house standard microscope method for measuring the cell diameter. The measurements are made on sectioned foams by searching for complete cells showing a typical dodecahedral structure. The data received for the cell (d_{cell}) and filament diameter (d_f) are an excellent fit to a simple linear model:

$$d_f = 8.860785 \times 10^{-6} + 0.075559 \times d_{cell} \qquad [1]$$

where both d_f and d_{cell} are in metres. This relationship provides a method, traceable to international standards, for estimating the filament diameters of the connecting elements in the porous foam matrix. Substitution into Vincent's model (and correction of the inconsistent units) gives for the particle penetration P through a foam

$$\ln(P) = -\frac{t}{d_f}\left\{5.486 St^{2.382} + 3.891 Ng^{0.880}\right\} \times 10^4 \qquad [2]$$

Where t is the foam plug thickness, d_f the equivalent filament diameter of the porous foam, St is the Stokes' number (inertial parameter) and Ng the gravitational parameter:

$$St = \frac{d_{ae}^2 \gamma U}{18 \eta d_f} \qquad Ng = \frac{d_{ae}^2 \gamma g}{18 \eta U} \qquad [3],[4]$$

Here d_{ae} is the aerodynamic diameter, γ the density of air, η the viscosity of air, U the velocity of air through the foam and g the acceleration due to gravity. In these equations all quantities (including the 'fibre' diameter) are in S.I. units.

This model has been implemented as an Excel spreadsheet (newmodel.xls, Kenny et al. 2001), utilising a macro (pencurv) to calculate the aerosol penetration curve for any specified foam, at any flow rate. The macro inverts the model, calculating aerodynamic diameter values corresponding to stated penetration values in an iterative manner. The inputs to the spreadsheet are the foam dimensions in mm, flow rate in litres per minute, and foam cell diameter values in µm. If the foam cell diameter values are not known, the spreadsheet calculates them from the stated porosity of the foam. The spreadsheet outputs aerodynamic diameter values in µm corresponding to penetrations ranging from 0.1 to 0.9, in steps of 0.1. Some typical examples of spreadsheet outputs are included in Figure 2 (respirable foams)

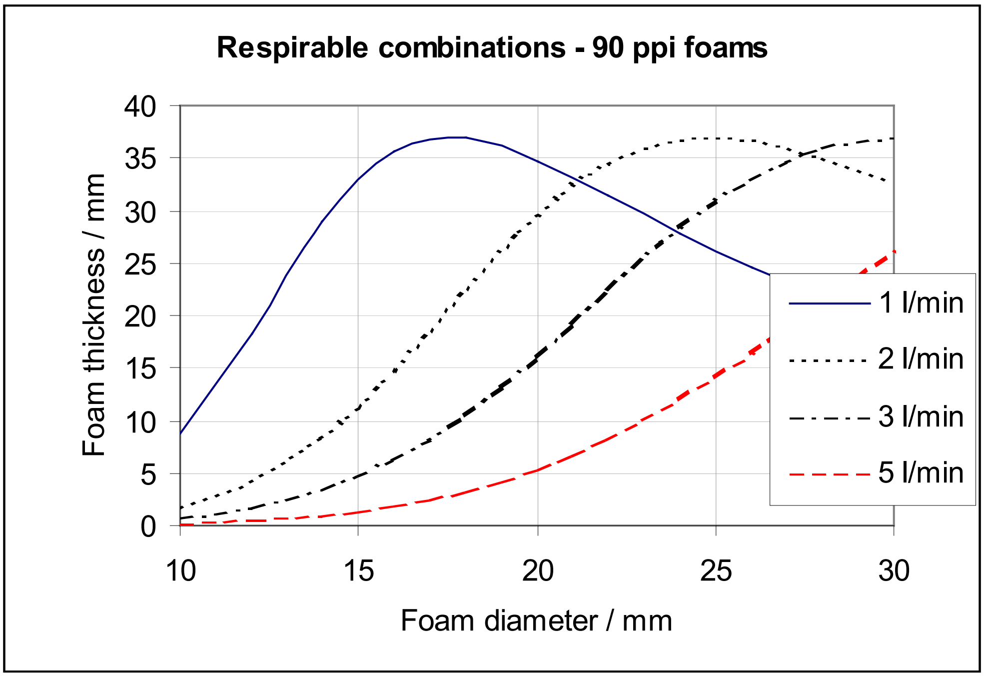

Fig. 2: Calculated foam geometries for respirable selection and different air flows

Many of the respirable solutions presented are too bulky for personal sampling, but it can readily be seen that the solutions are constrained by the availability of suitable foams. The highest porosity non-compressed foam is around 90-100 ppi, whereas the lowest porosity compressed foam is around 170 ppi. Ideally, a foam with porosity within this range would be suitable. The thoracic solutions are more compact, however, thoracic solutions with thickness below 10 mm are probably ineffective at retaining particles. For typical personal sampling flow rates, there are only a few dimensional combinations that are likely to give adequate performance. Foam porosities ranging from 35 ppi to 55 ppi are of most interest.
The spreadsheet enables the user to investigate the potential aerosol sampling errors that would result from a mis-match between the foam module specification and the actual supply. In general, foam dimensions can be cut to ±1 mm, and flow rate can be controlled to better than ±0.1 l/min. The precision on determining the cell diameter can be estimated to ±10% (although note that a ±10% error in cell diameter translates to an error of only ±3 ppi for a 35 ppi foam). It is clear that the cell diameter error has the largest effect, two to three times that of the other two errors (plug thickness, flow rate).

The spreadsheet was used to compare model predictions with foam penetration data for existing modules, designed using an experimental trial-and-error process. When the model is implemented correctly its predictions for the penetration curves of existing foam modules are in good agreement with experiment. The aerodynamic diameters corresponding to a given penetration in general agree to within 5%. To obtain foam modules that have the required aerosol size selective behaviour, it will be necessary to place tolerances of ± 5% on the cell diameter. This will require new supply arrangements since the former vendors did not use the cell diameter information, and could not supply such closely-specified foams.

6 Particle penetration through foams

6.1 Experimental set-up

Different methods for testing the particle penetration through porous foams were applied, one used by HSL and described by Kenny and Stancliffe (1998). Another similar set-up was used at IOM which is described below. A third set-up with a low speed wind tunnel was used at INRS (Görner et al. 2001).
They all have in common the same kind of challenge aerosol (glass beads) and the same kind of particle detection unit (TSI Aerosol Particle Sizer APS, different versions). The basis of the approach is the real-time sequential measurement of the concentration and aerodynamic size distribution of the challenge and penetrant aerosol for a sample (in this case a porous foam plug) under investigation. For each size interval in the distribution, the ratio of the penetrant to the challenge aerosol provides a measure of the efficiency. Using the efficiency data for each size interval an efficiency function may be evaluated. This function may then be used to evaluate indicators of performance such as d_{50} or to test the match against the particle sampling conventions. This approach provides a rapid determination of the efficiency function.

The design of the system at IOM is based on that described by Kenny and Liden (1991) used for the measurement of aerosol penetration through cyclone samplers. Further adaptations of the approach have been described by Maynard et al (1999).

The experimental system comprises the following components; aerosol, aerosol generator, exposure chamber(s), measurement system and analysis system (Fig. 3).

Aerosol: The specifications of the test aerosol are that it should be inexpensive, polydisperse with a broad size distribution, spherical and have minimal surface irregularities. Two candidate aerosols were identified, both solid soda glass ballotini, (i) Grade 5210 supplied by Jencons Scientific UK Ltd. which has a specific gravity of 2.50 - 2.55, a physical diameter of 0 to 50 µm and is available in kg sized packs and (ii) Grade 5000 CP00 supplied by OMYA Croxton and Garry (C&G) with similar physical specifications.

Aerosol generator: The aerosol generator used is a TSI fluidised bed (Type 3400). In this compressed air is used to generate the fluidised bed, comprising a mixture of large (200 µm) phosphor bronze spheres and the test material, and to transport the test aerosol, via a copper tube to the exposure chamber. A mixed ion source is placed in the feed line to establish a Boltzmann distribution in the test aerosol.

Exposure chamber: The exposure chamber is shown in schematic form in Figure 3 along with the rest of the experimental set-up. It comprises a 1 m^3 enclosure into which the aerosol is fed. Mixing is provided using a baffle arrangement. This has been shown to produce a satisfactory spatial distribution for particle aerodynamic diameters 1 to 20 µm. The exhaust flow at the base of the chamber is balanced to maintain a slight negative pressure in the chamber. The foam sample piece under test is placed in the foam holder. Measurement of the penetration characteristics of foam samples is carried out by comparing the aerodynamic size distribution and concentration of a sample passing through the foam with that of the challenge aerosol collected through the open sampler alongside. Details of the foam holder and challenge sampler are given in Figure 4. A different foam holder is required for each diameter foam sample to be tested. In each case, the challenge sampler has identical entry diameter (d) and entry length (l_e). The total length of the foam holder is the entry length plus the foam thickness (l_t). Air is drawn through the sample holder by the Aerodynamic Particle Sizer (APS) integral pump and flow control system. Using the two ball valves at the base of the chamber allows either foam filtered sample or the challenge sample to be selected.

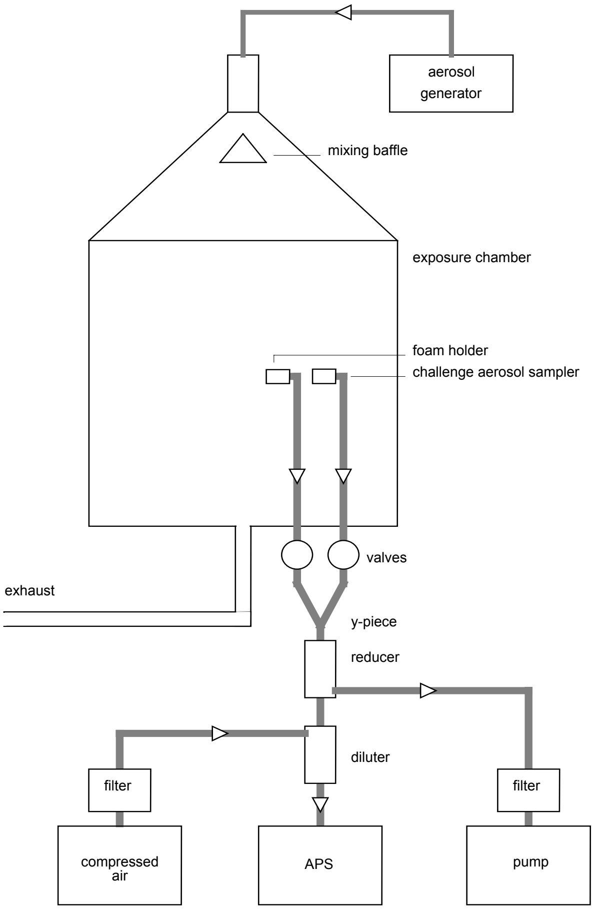

Figure 3 Experimental test system

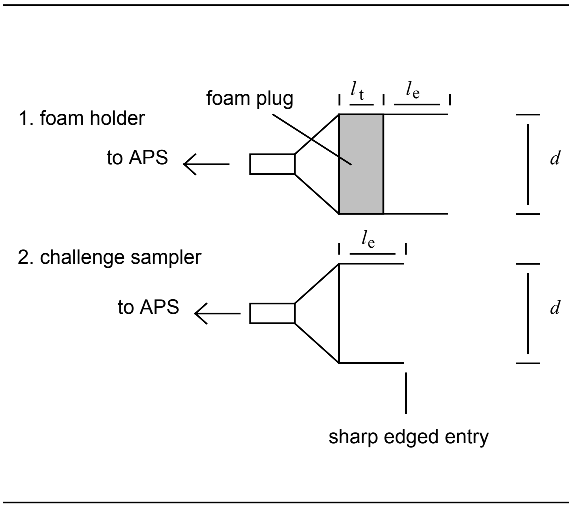

Figure 4 Foam plug holder and challenge aerosol sampler

Measurement system: After passing through the selected ball valve, the sample is drawn through a Y-piece into the rest of the measurement system. The APS measurement system has a fixed sampling rate of 5 $lmin^{-1}$. For sample flows greater than 5 $lmin^{-1}$, the flow reducer is used. The TSI Aerodynamic Particle Sizer Model 3320 measures the aerodynamic size distribution of the sampled aerosol in the size range 0.3 to 20 µm by measuring the time-of-flight of individual particles as they pass through two sections of a split laser beam. The measured size distribution is stored for subsequent analysis on a companion PC using the Windows based *Aerosol Instrument Manager™* software.

6.2 Comparisons

Using this test system work was carried out to examine the various parameters considered as potential factors in penetration. These included face velocity, porosity, orientation, flow rate, diameter, thickness, coating, loading and charge. As an initial step, it was considered important to carry out some comparison of the results obtained in the new system and those obtained in other participating laboratories. The difference between the IOM data and the HSL/INRS data had not been resolved and remained of the order of 10 to 20%, which may be due to different versions of the APS measuring system. A comparison of experimental data from HSL and INRS with the penetration model from Vincent et al. (1993)was done, including the calculated model aerodynamic diameters corresponding to penetration values between 0.1 and 0.9 (in steps of 0.1) for each of the foam specimens tested.
Figure 5 shows the measured aerodynamic diameters plotted against the model aerodynamic diameters for a 84 ppi foam. The graph includes both HSL and INRS penetration data.

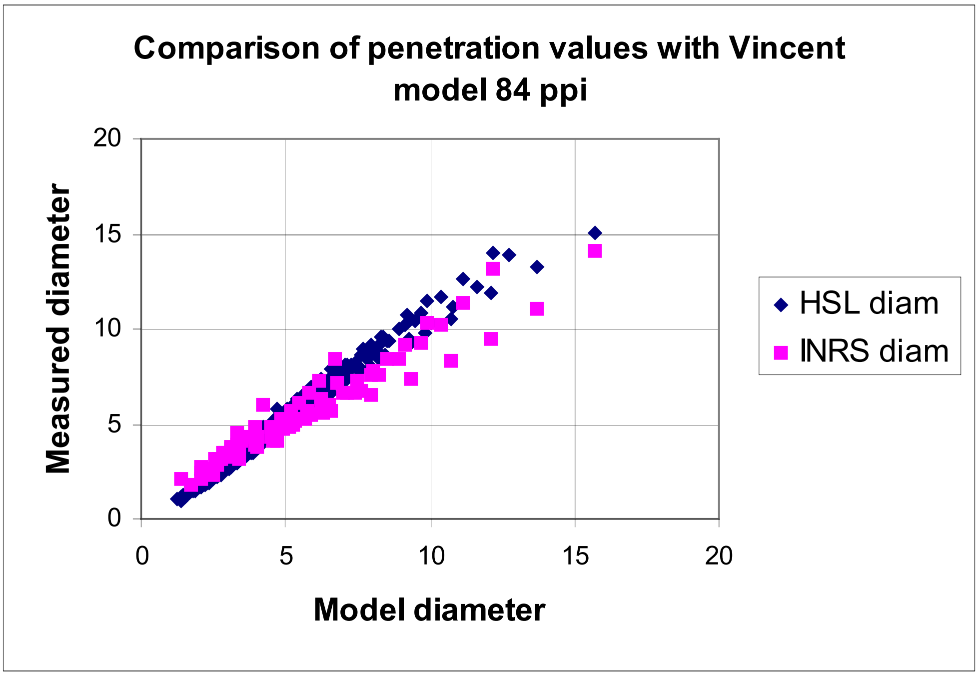

Fig. 5: Penetration of particles through a foam of 84 ppi, comparison of measurements and calculations

Comparison of the data for the three foam grades (35, 84, 170 ppi) indicates that there is no significant difference in the measured-model relationship for each grade. This means the model description is also useful for higher-porosity foams, higher flow rates and small foam pieces than the original model was developed for.

Hence the data from the three foam grades can be pooled together in order to obtain a functional relationship relating the model diameters to the measured diameters. The pooled data may be fitted by a simple line:

Measured diameter = 1.05 × model diameter

However, in the context of the difficulty in obtaining foams with a precisely known porosity or cell diameter, the factor of 1.05 is if little importance. Hence the conclusion that must be drawn is that the existing Vincent *et al.* model already provides an adequate description of the foam penetration values measured in this project. In the circumstances there does not appear to be a case for replacing the model with a new one, except for the reformulation discussed above.

6.3 Influence of coating

It has been shown, that to maximise the adherence of particles on to some foam plugs, it is necessary to coat the surface of the foam plug filaments with a tacky substrate. In previous studies (Aitken and Donaldson 1994) it has been shown that application of petroleum jelly is effective in this respect. This is applied by immersing the foam plugs in a solution of petroleum jelly dissolved in xylene or some other suitable organic solvent. It has also been shown that coating was only required for plugs designed to separate the thoracic fraction. Experiments included foams of 100 ppi porosity, 10 mm diameter and 5 mm thick, coated with 3 % petroleum jelly in xylene, tested at 1 l/min air flow. Although coating is primarily used on foam plugs designed to separate the thoracic fraction, the plugs used in this experiment were samples designed for separation of the respirable fraction. Since these plugs have much smaller pore size, it was considered the relative influence of coating would be greater (and so easier to measure) in this case. The results of d_{50} clearly indicate that the difference in penetration between these coated and uncoated foam plugs is not significant (reduction from 3.87 to 3.83 µm). We conclude that coating using the method described does not influence the penetration through foam plugs to any significant extent.

6.4 Influence of foam loading

Clearly, as deposited material builds up within foam plugs there is a potential that this material will effectively alter the diameter of the foam plug filaments and so alter the selection characteristics. Pre-loaded foam plugs were prepared by aspirating through the plugs, in holders, in an aerosol of F 1200 grade aloxite, in a small wind tunnel. Two designs of foam plugs were used, each of which had a nominal d_{50} of 4 µm.

i) 100 ppi, 10 mm dia x 5 mm thick, flow 1 l/min, face velocity 0.06 m/s
ii) 100 ppi, 30mm dia x 25 mm thick, flow 2.5 l/min., face velocity 0.2 m/s.

Again, as in the case of the coating experiments (previous section), it was considered that plugs designed to measure the respirable fraction would provide a “worst-case scenario”. The summarised results are shown in Figure 6, showing measured d_{50} plotted as a function of mass load.

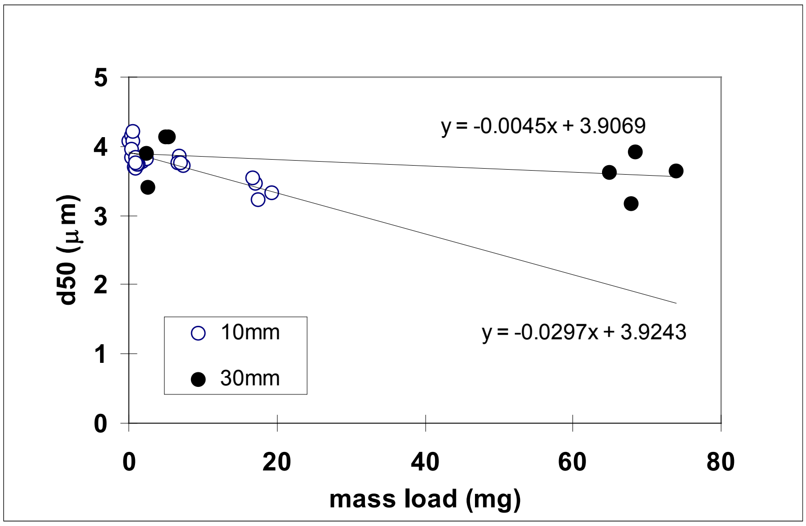

Figure 6 **Measured d_{50} plotted as a function of mass load for two foam designs**

Figure 6 gives a good indication that mass loading does have an effect on the penetration of particles through the foam plugs. For both foam plug geometries, there is an evidence of a decrease in the measured d_{50} which to a fair approximation may be regarded as linear. It is also clear that the influence of loading appears different in the two foam plug geometries, not surprisingly, the effect being much larger in the smaller foam plugs. For each configuration we have derived a functional relationship. Based on that we can evaluate the probable change in d_{50} associated with an increase in mass loading. It maybe seen that for the 10mm plugs a mass load increase of 10mg would reduce the d_{50} from 3.92 micron to 3.63 microns, a decrease of some 7%. Similarly for the 30mm diameter plugs, a mass loading increase of 10 mg would result in a decrease in the d_{50} from 3.91 microns to 3.86 microns, a decrease of approximately 1%.

These changes, although significant, may have little practical importance. When used in real workplaces, it is unlikely that sampling instruments using such foams as collection substrates, will collect 10mg over a single shift.

6.5 Influence of electrostatic charge

Capture of particles by foam plugs due to electrostatic processes had not been considered in the previous experiments, although due to the non-conducting nature of the foam plugs, the possibility of charge effects does exist. By comparing the selection characteristics of foam plugs challenged by an aerosol which has been neutralised through injection of air ions, with those of plugs challenged by a non-neutralised aerosol, we determined whether the presence of electrostatic charge has any effect on penetration. The plug design used had a nominal d_{50} of 4 microns. As additional variable the foam cassette was electrically earthed. The results clearly indicate that no differences between those plugs exposed to untreated aerosol in earthed, and in non earthed cassettes, was found. In each case the mean d_{50} was measured at 3.80 microns. The measured d_{50} for the neutralised aerosol was 3.98. This is slightly larger than the mean of the D50s measured for the untreated aerosol. Though significant this difference is small at less than 5%. Again given that this is likely to be a worst case scenario, we conclude that the presence of electrical charge is not likely to produce a significant effect on the performance of foam plugs.

7 Design of foam modules and prototype samplers

For later applications of a three-stage personal air sampler it was necessary to develop and design new foam holders to fit into the basic inhalable dust samplers IOM and PGP-GSP. According to the theoretical model described above several solutions for the foam geometries could be found. The cell diameters 1643 and 470 µm were chosen according to the available foam samples. In this case only the 20 mm diameter thoracic foams will be useful for the PGP-GSP. Table 3 gives the calculated dimensions of suitable foam plugs for the two sampler air flows, thoracic and respirable dust selection and different foam diameters.

PGP-GSP 3.5 l/min	d_{50}	D_{cell}	Diameter	Thickness
	µm	µm	mm	mm
thoracic	11	1643	20	7.5
respirable	4.3	470	20	15.6
IOM 2 l/min				
thoracic	11	1643	15	7.2
respirable	4.3	470	15	15.1

Table 3: Calculated foam plug dimensions

But the results of modelling also show the biggest problem in getting a good fit to the theory: the availability of foams with precise cell diameter. If the cell diameter is not well adjusted the thickness of the foam plug will not be in a suitable range for use in the holders or will probably be too small in case of the thoracic selection. In this case particle loss towards the respirable foam could be increased. Thickness of the thoracic foam is thought to be at least 10 mm to avoid this effect. Cell diameters of 1850 and 440 µm would give better foam plug dimensions and should be preferred, if the manufacturer can supply these.

Choosing these foam dimensions, suitable adaptors for the IOM and PGP-GSP inhalable samplers were designed and manufactured. Fig. 7 shows the prototype versions of the three-stage samplers IOM-ITR and PGP-ITR which had to be tested in further trials as described below.

Figure 7: Prototypes for three-stage dust samplers: IOM-ITR in front row and PGP-ITR in back row.

8 Test of filter modules and prototype samplers

The performance data for module design obtained in this process was assessed against the relevant target convention in EN 481, using the bias map approach described in EN 13205 (CEN 2001). For each module the bias between the fitted performance curve and the target convention for an array of challenge size distributions, specified in the EN was calculated. The standard states that a sampler (in this case, module) is in conformance, if 85% of the results lie within the agreed boundary, in this case a bias of ± 10%. The fraction of distributions which lie within the agreed boundary is known as Bias Performance Criterion (BPC).

In total 5 different modules to be used in the IOM-ITR and PGP-ITR samplers were taken into account. These also allow to combine different versions of prototype samplers which also were tested partially to determine their efficiencies.

Full detailed results for single fraction modules were obtained, including the evaluation and plots of penetration as a function of d_{ae}, the measured d_{50}, bias maps and evaluations of BPC. Based on consideration of these results obtained, the recommended design configurations for the modules are as follows;

Sampler type	Dust fraction	Foam cell diameter	Foam thickness	Foam diameter
		µm	mm	mm
IOM-ITR	thoracic	1638	13	16
IOM-ITR	respirable	421	11.5	17
PGP-ITR	respirable	421	11.5	22
PGP-ITR	respirable	472	3.6	16

For the thoracic module of PGP-ITR, four designs were evaluated, none of which were acceptable in terms of BPC. All of the designs tested appeared to have large positive biases for larger particles (greater than 20 µm). However, the PGP-ITR thoracic results need to be interpreted with some caution (and to some extent, the IOM thoracic results). The APS measurement had an effective upper limit of 15 µm and for many of the experiments there is a paucity of data in this size range and so these positive biases are derived from extrapolations of the penetration curve. In addition, the count statistics were very poor at all sizes above 12 µm.

Laboratory measurements of sampling efficiency of the entire aerosol samplers equipped with only one foam module was done in a low-speed wind tunnel (wind velocity W ≈ 15 cm/s) with aerosol generation at INRS. The wind tunnel facility is described in Fabriès et al. (1984). The sampler is placed inside the tunnel in a homogenous aerosol ambience. The aerosol is sampled by the candidate sampler and by a reference sampling orifice with an efficiency assumed to be close to 1 for each particle size from the aerosol distribution. The particle size-dependent concentrations of the ambient aerosol $C_a(d_{ae})$ and the sampled aerosol $C_s(d_{ae})$ are measured and the sampler efficiency $E_s(d_{ae})$ is calculated as follows:

$$E_s(d_{ae}) = C_s(d_{ae}) / C_a(d_{ae})$$

where d_{ae} is the aerodynamic diameter of the particles.

The APS (Aerodynamic Particle Sizer 3300, TSI inc. St. Paul, MN, USA) method of aerodynamic particle size analysis was used (Fabriès et al. 1998, Baron 1986).

The dimensions of the modules inserted in the samplers and the results are reported in Table 4 and Fig. 8.

Table 4 Porosities and dimensions of the particle-selecting foam modules and the experimental d_{50} cutpoints of the samplers. Conventional and expected d_{50} cutpoints are also reported.

Exp. work INRS **2001**	Thoracic fraction	Respirable fraction
Foam porosity	45 ppi, $d_f = 158.59 \pm 4.76$ µm $d_c = 1634 \pm 96$ µm	90ppi, $d_f = 47.13 \pm 1.17$ µm $d_c = 476 \pm 36$ µm
IOM-ITR sampler Dimensions of foam modules Experimental d_{50} cutpoint	 D = 15 mm ; L = 14 mm d_{50} exp.= 12.33 µm	 D = 15 mm ; L = 16 mm d_{50} exp.= 5.16 µm
PGP-ITR sampler Dimensions of foam modules Experimental d_{50} cutpoint	 D = 20 mm ; L = 9 mm d_{50} exp.= 10.58 µm	 D = 20 mm ; L = 16 mm d_{50} exp.= 4.84 µm
Expected d_{50} cutpoint	d_{50} = 11.0 µm	d_{50} = 4.3 µm
Conventional cutpoint [CEN 1993]	d_{50} = 10.0 µm	d_{50} = 4.0 µm

The efficiency of an ideal sampler would match the conventional target curve exactly and the experimental d_{50} would be equal to the conventional d_{50}. In the case of an experimental efficiency curve with a sharper slope it can be shown by numerical simulation that the global sampling performance may be better with a d_{50} cutpoint slightly higher than the conventional one. This cutpoint is called "expected d_{50}" in Table 4.

The measured experimental efficiency data of the sampler prototypes are plotted in Fig. 8 along with the CEN-ISO-ACGIH conventional penetration curves. The average experimental d_{50} are also reported.

The conventional sampling condition is fairly well satisfied in the case of the PGP sampler, particularly in its thoracic version. In the case of the PGP respirable sampler and the IOM sampler in both versions, the experimental sampling efficiency presents a slightly higher slope and higher d_{50} than expected. The design of both samplers does not allow for a further change of geometry or flow rate of the foam modules. A slight modification of foam porosity could be a means to improve sampling efficiency but this depends on the foam manufacturer. The bias maps show that the IOM sampler is well suited for sampling the thoracic and respirable fractions in the case of fine aerosols. The respirable fraction can also be successfully sampled in certain coarser aerosols. The PGP thoracic sampler has an excellent performance for any aerosol distribution and the PGP respirable has a very good performance for 63% of the aerosols within the bias map. Even for the rest of aerosol distributions its bias does not exceed 20%.

The performance expressed in terms of accuracy seems to be better in all cases. This is due to the fact that the accuracy requirement is less severe (30% accuracy tolerance) than the bias requirement (± 10% bias tolerance). Taking into account that the accuracy is composed to a great extent of the absolute value of bias (CEN 2001), a more reasonable accuracy requirement would be 20%.

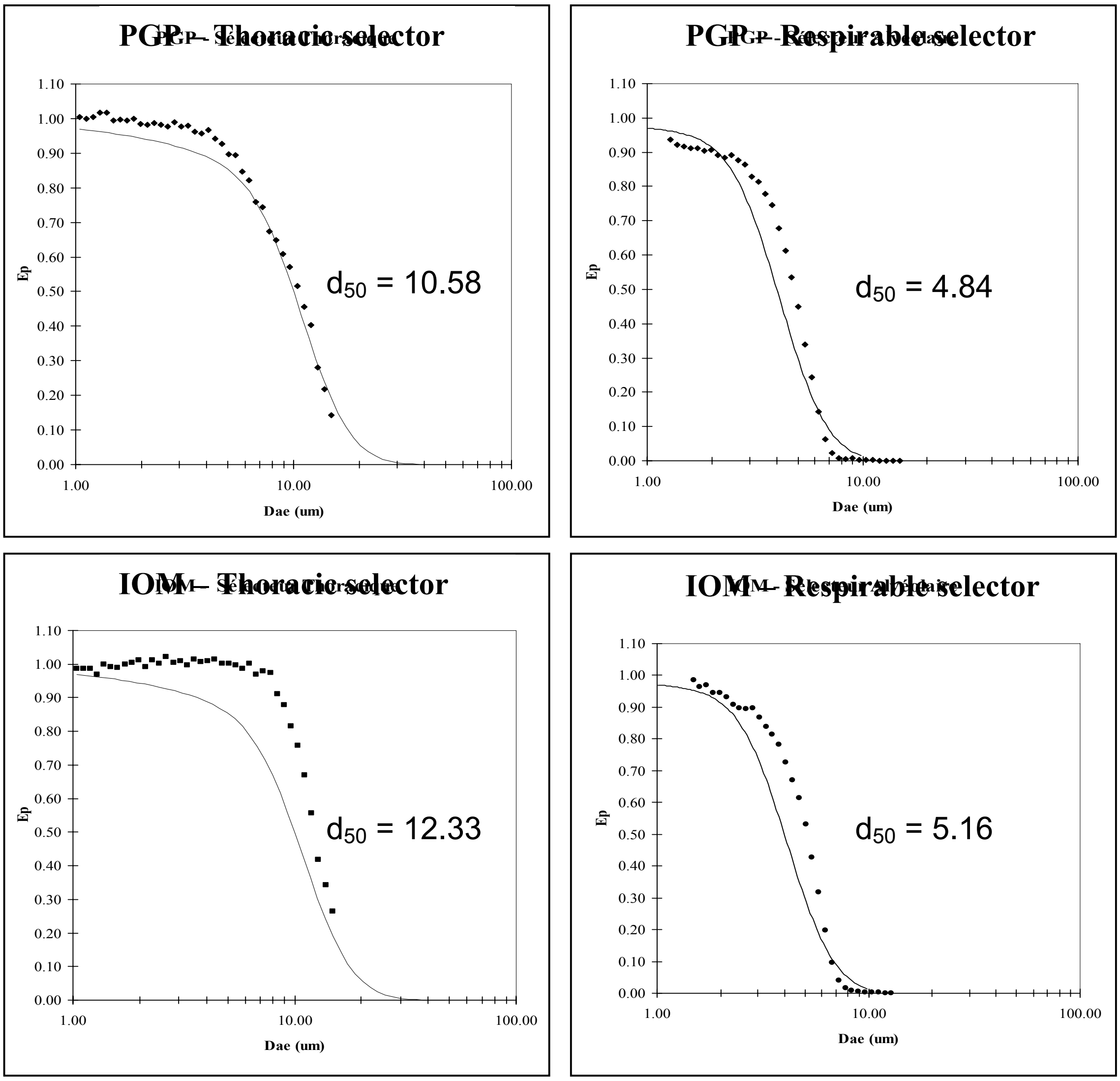

Fig. 8 Size-dependent experimental sampling efficiency of the thoracic and respirable versions of the IOM and PGP multi-stage samplers. Experimental measurements 2001. Continuous lines represent the CEN-ISO-ACGIH conventional penetrations.

9 Analysis of loaded foams

9.1 Weighing of foams

Usually an overall dust concentration will be calculated from the sampling time and the sampled mass on the filter. The mass is determined by weighing the filter before and after sampling under stable conditions like temperature and humidity. The foam has a rather large surface on which humidity and other condensing substances will adhere. The weight stability due to the influence of humidity was determined quantitatively by using a climate chamber with different humidity concentrations and measuring different foam porosities. The weighing procedure will be useful for the determination of inert dust concentrations, especially in workplaces with high dust concentrations or for sampling over a long period of some hours. A three stage sampling system will be advantageous, because overloading will occur later in comparison to an one stage sampling.

9.1.1 Preparation and weight stability

In order to supply clean PU foam plugs it is necessary to perform a washing procedure. The following steps show sufficient good results for using foams:

1. After cutting the foam sheets into plugs of desired diameter, take hand-warm water with a drop of detergent. Wash the foams several times in this liquid. Application of ultrasonic devices is also possible.
2. Remove the foams from the water and squeeze out excess liquid
3. Rinse the foam by immersing in de-ionised water
4. Remove and squeeze out the excess
5. Repeat rinsing with de-ionised water 5 times using clean water on each occasion
6. After final rinsing, dry the foams for at least 12 hours at temperatures up to 70°C in a clean vessel placed in an oven.
7. Store the clean foams in clean vessels for later use.

This cleaning procedure is not suitable if the foams are used for the analysis of organic compounds (as explained later).

In order to determine the precision for weighing foams, experiments at IST were carried out in a glove box with controlled temperature (Peltier element with small fan) and humidity (saturated salt bath with $Ca(NO_3)_2 \cdot 4\ H_2O$, stable relative humidity of 51 %). Controlling the temperature and humidity reduces the repeatability from 0.07 mg to about 0.005 mg, at 2 min equilibrium time for the balance. A Mettler M3 microbalance with 1µg resolution was used. The humidity changed from 48 to 55 %.

If this standard deviation of the unloaded foam is taken as basis for the uncertainty, the limit of detection (LOD) can be estimated as 3 times this standard deviation and the limit of quantitation (LOQ) as 10 times this standard deviation.

LOD = 0.015 mg
LOQ = 0.050 mg

Different experiments in BIA with a Sartorius 1712 MP8 balance in a laboratory room with 37 to 45 % relative humidity and temperature between 23 and 24 °C gave the following results (Table 5):

foam type	cell diameter	plug diameter	plug thickness	total mass	standard deviation
	µm	mm	mm	mg	mg
respirable foam	470	15	3.6	21	≤ 0.018
respirable foam	470	15	11.8	62	≤ 0.012
respirable foam	470	20	11.8	108	≤ 0.023
thoracic foam	1643	20	10	95	≤ 0.015

Table 5: Mass deviations of unloaded foams

The relative standard deviation is always less than 0.1 % of the total foam plug weight. Assuming the largest standard deviation of 0.023 mg the limits of detection and quantitation will be

LOD = 0.069 mg
LOQ = 0.230 mg.

This is nearly five times as high as under controlled climate in a glove box, but still lower than the LOD of a cellulose nitrate filter.

For 37 mm diameter cellulose nitrate membrane filters and glass fibre filters, commonly used in the PGP-GSP sampler, the LOD is 0.3 mg as quantified by BIA under climatised room conditions (typically ± 5 % rel. humidity).

Taking into account the thoracic and inhalable fraction to be measured with the three stage samplers more than one uncertainty have to be combined. As the thoracic part of a sampler consists of a foam plus a membrane filter and the inhalable part of two foams and one membrane filter the resulting uncertainties are a sum of the single uncertainties. They are estimated in Table 6. They can be decreased in using a better controlled climate like in a glove box.

	LOD	LOQ
selector	mg	mg
foam	0.069	0.23
membrane filter = respirable fraction	0.3	1.0
fraction		
thoracic	0.369	1.23
inhalable	0.438	1.46

Table 6: Uncertainties for the three-stage foam samplers (LOD: limit of detection, LOQ: limit of quantitation)

The weight curve of a desiccated foam of 45 ppi porosity revealed a weight equilibrium after about 1.5 hours. The 100 ppi foam reaches equilibrium in about 3.5 hours, an 80 ppi foam in about 2 hours. These results indicate, that an adaptation time to surrounding humidity of about 4 hours will be sufficient. In general laboratory practice a storage time of 12 to 24 hours before weighing is common use. This will assure all foam porosities to reach equilibrium mass due to different humidity.

9.1.2 Humidity dependence

In general form the mass M of a foam at relative humidity rh can be approached by the linear relationship

$$M = A \cdot rh + M_0$$

with A as slope factor in g/%, rh as relative humidity in %, M_0 as dry weight (rh = 0 %) in g.

Figures 9 and 10 illustrate the mass of two uncoated foam plugs in dependence of the relative humidity in the laboratory room. Each mass value represents a mean value from 5 single mass values.

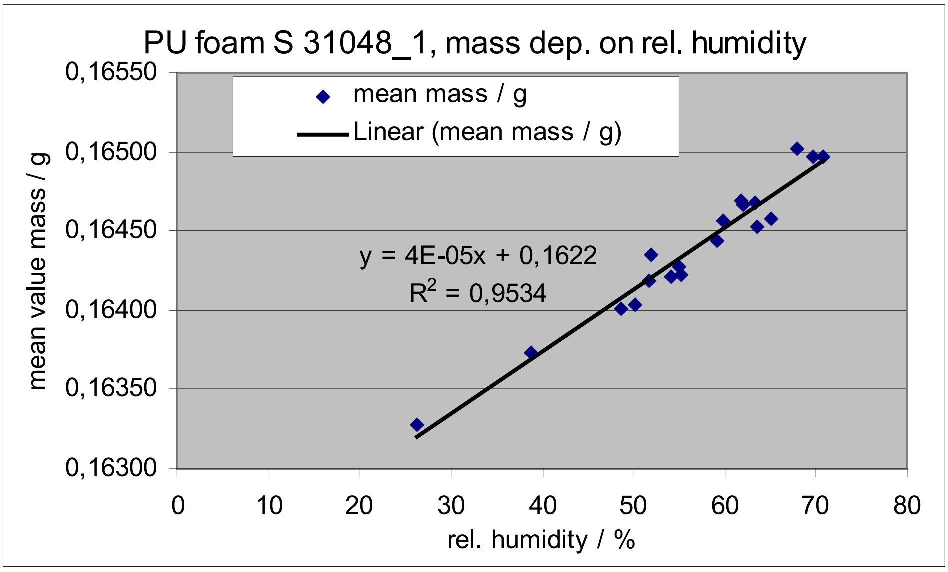

Figure 9: Change of mass of a respirable foam with 476 µm cell diameter, 21.8 mm diameter, 16 mm thickness

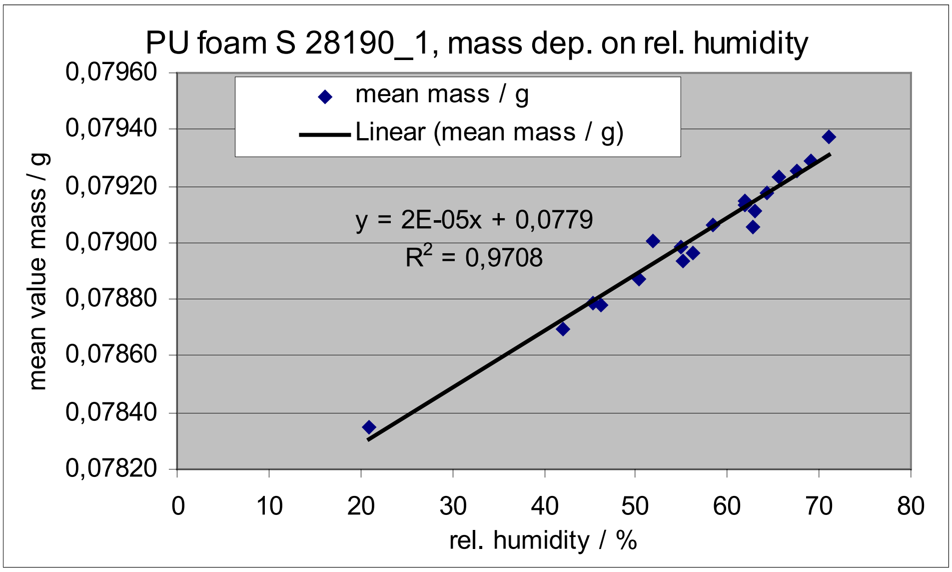

Figure 10: Change of mass of a thoracic foam with 1611 µm cell diameter, 22 mm diameter, 9 mm thickness

The measured values A, M_0 and A/M_0 for the two above foams are given in Table 7. The slope A depends mainly on the inner total surface of the foam plug and $A \cdot rh$ represents the adhered water vapour, but only for the given plug characteristics (geometry and porosity).

Foam	cell diameter	diameter of plug	thickness of plug	A	M_0	A/M_0	A/N_C
	µm	mm	mm	g/%	g	1/%	g/%
S28190 uncoated #1	1611	22	9	$2 \cdot 10^{-5}$	0.0779	$2.57 \cdot 10^{-4}$	4.02E-08
S31048 uncoated #1	476	21.8	16	$4 \cdot 10^{-5}$	0.1622	$2.47 \cdot 10^{-4}$	1.19E-09

Table 7: Foam mass dependence on humidity for uncoated and coated plugs

The densities of the foams are 28 kg/m³ for the S 28190 and 31 kg/m³ for the S 31048. A measure to describe the dependency of A on porosity would be the value A/N_C with N_C as the number of cells in the volume of the whole plug. A/N_C represents the weight change in g per cell per % of change of humidity and thus is a small value. N_C is calculated as $N_C = V_{plug} / V_{cell}$.

It can be seen that large cells (e.g. S 28190) have a larger weight variation in humidity, given by the parameter A/N_C. The mean values for A/N_C are $4.12 \cdot 10^{-8}$ and $1.19 \cdot 10^{-9}$ g/%, respectively.

If the foams are coated by using solutions of Vaseline in xylene at 3 weight-% or 10 weight-% no evidence can be seen for a different humidity behaviour than the uncoated foams. The parameter A/N_C is nearly unchanged.

9.1.3 Particle fall-off

Former studies at IOM in the nickel industry study showed particle fall-off when a cassette with loaded foam was knocked or roughly handled. Almost porosities of the thoracic foams and large particles greater than about 10 µm are affected. As this fall-off could not be controlled by a handling protocol in field use or transportation of the cassettes other ways to prevent this should be applied. Only the coating of coarse foams was seen to be a relevant solution. A dissolution of 3 and 10 weight % Vaseline (paraffins) in xylene was used for immersing the foam plugs. After evaporating of the xylene the Vaseline grease acts as sticking surface. Performing a drop test of dolomite loaded thoracic foams (50 drops of 2 cm height in series) revealed mean values of mass loss. They indicate the decrease of loss with increasing Vaseline coating. The uncoated foams have 55 % loss in mean, the 3 % coated only 17.5 % and the 10 % coated 7.4 %.. This means that coating with 3 % Vaseline shows a reduction of factor 3, coating with 10 % a factor of 6.

9.2 Chemical analysis of inorganic compounds

Most airborne hazardous substances have single limit values, so that direct chemical analysis is advantageous. To apply such procedures for loaded foams, suitable methods for recovering particles and condensed compounds from the foam material need to be developed. The application of existing standard methods for the analysis of selected trace metals and organic workplace pollutants is the main intention. The advantage is that the methods are validated and are under control. However the conditions for their applications to the foam materials are verified.

The determination of inorganic compounds is mainly performed with ICP-MS (inductively coupled plasma – mass spectrometry) or AAS (atomic absorption spectrometry). These standard procedures used in laboratories of BIA and IST can roughly be described as follows:

Solubilization by acid digestion

- ☐ Procedure A. According BIA standard method.
  - Acid dissolution (25 % HCl, 65 % HNO_3, 1+2)
  - The suspension of PUF in acid is refluxed for 2 h
  - Destruction of foam matrix, formation of fine particles
  - Dilution (minimum 1:4) with water for quadrupole ICP-MS

- ☐ Procedure B. According to IST methods.
  1. Variant B1. 10 mL nitric acid >69.5% + 5 mL hydrogen peroxide 30% Suprapur + 5 mL bidistilled water overnight.
  2. Variant B2. The digestion (1 gram of PUF) is made with concentrated nitric acid in a teflon autoclave at 120°C (Parr bomb). A final suspension of black particles turned out to be a clear solution after centrifugation. Subsequent dilutions are made for determination by AAS.

In a first step blank foam plugs were analysed for their inorganic impurities. Three different foam batches had been under investigation: (i) 60 ppi, delivered from Foam Engineers, UK, originating from Recticel, (ii) 10, 80 ppi, from Nauer, CH, (iii) Recticel Bulpren, 470 and 1625 µm cell diameter. Three elements could be found in significant amounts.

Tin (Sn)	5.6 to 200 µg/g foam
Calcium (Ca)	27 to appr. 520 µg/g foam, with large variations of appr. ± 20 %
Magnesium (Mg)	5.4 to 65 µg/g foam

Nickel and lead and other elements ranged below the limit of quantitation in case of ICP-MS.

Detection limits:

B, Ti, Fe:	10-20 µg/g
Ba, Pb, Cr, Ni, Zn, Se, As, Pa:	3-5 µg/g
other (Cd, Sb, Ta, Wo, Pt, Tl, Mn, Co, Cu, Sr, Zr, Nb, Mo, Ag, Rh):	1-2 µg/g

For AAS the limit of quantitation was for Ni 25 µg/l or 5 µg/g of the sample and for Pb 10 µg/l or 0.55 µg/g of the sample.

At this stage, the polyurethane foams investigated can not be recommended for the chemical analysis of calcium and tin. The foam material itself contains higher blank values of Ca and Sn with especially high variations of Ca. The high variations of Ca can also be caused by manually washing the foams before sampling.

in order to determine a recovery rate of Ni and Pb, resp., the spherical glass particles were coated with a Ni and Pb solution and dried. Then this dust was sampled with a foam. Analysis of Pb and Ni in the foam matrix are straightforward according to the AAS method described.

The weight levels of Pb and Ni on the Spheriglass particles (mean of three random samples) are taken as "true values":
Pb = 5.76 % ± 4.2%
Ni = 4.91 % ± 2.6%
The determinations in about 10 samples of foam (35 ppi) after dynamic loading with the impregnated particles shows that the differences between the "true value" of Pb and Ni (deducted from gravimetric measurements) and those obtained from AAS analyses are <17 and <10 % respectively. In terms of demonstration of analytical validity, within experimental errors, this shows that the acid decomposition of foam is sufficient and that there are no observed interferences by the foam matrix. With the 90 ppi foam, this experimental design is not best suited for the analytical validation since the much smaller particles contribute less to the weight and therefore the observed differences are about 50% between "true value" and analytical values. Of course, the future analytical validation of foam samplers should be made with dusts in the workplace especially in atmospheres polluted by the metallic aerosols.

9.3 Chemical analysis of organic compounds

9.3.1 General treatment of foam for the determination of organic compounds e.g. polycyclic aromatic compounds and isocyanates

A two-step cleaning procedure is devised for the foam pieces intended for the sampling of adsorbed organic particles in the workplace atmosphere.
Following the cleaning with water and detergents as described, the foam materials are put in 30 ml of an organic solvent and ultrasoniced in an ultrasonic bath for 15 min; the operation is repeated. Except for dichloromethane and acetonitrile, our investigation shows that the initial pore size integrity of the foam is not affected by solvent cleaning with hexane, cyclohexane, toluene, acetone, methanol. The variation of cell diameter is equal or less than 5% (within the variation of the measurement method) in comparison with the cell diameter of a non treated foam. The foam pieces may change their physical aspect after solvent cleaning (swelling) but recover their initial visual aspect after air or oven drying.

9.3.2 PAH detection

Fig. 11 shows the HPLC fluorescence chromatogram of the 16 standard PAH coated on the Spheriglass particles, extracted and analysed by IST method . The chromatogram of the foam blank appears free of interferences for the carcinogenic PAH like benzo[a]pyrene, benzo[ghi]perylene or dibenzo[a,h]anthracene. Limits of detection are below the nanogram range and are to be defined as a function of operating parameters. Due to the sensitivity of the fluorescence detection, nanogram per cubic meter is easily achieved.

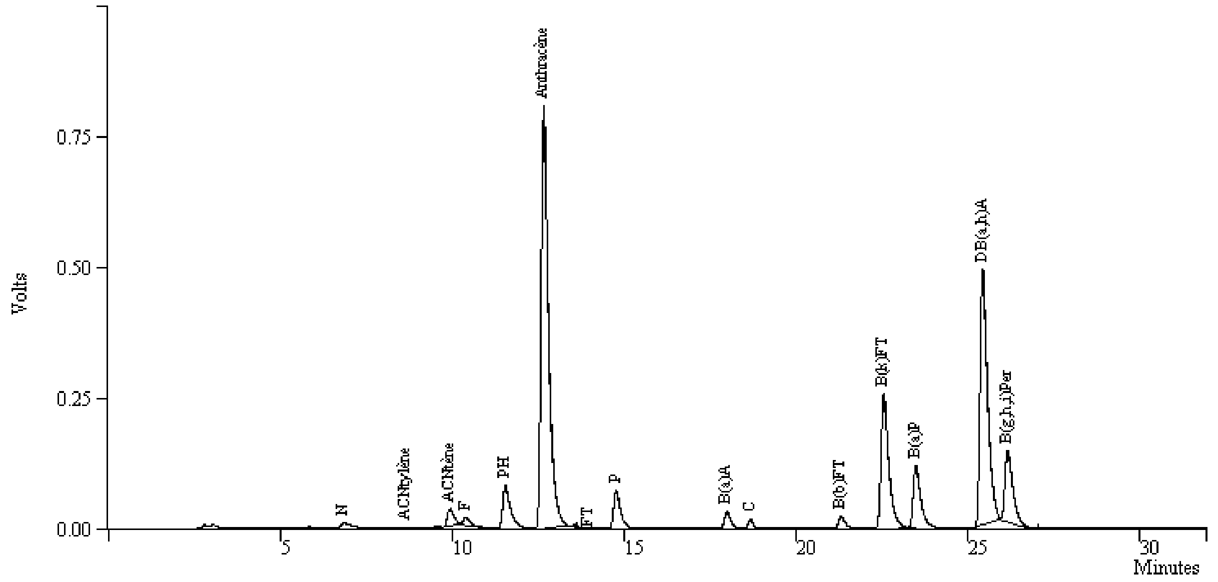

Figure 11: HPLC-Fluorescence profile of PAH mixture on PU foam

Details of operating procedures for HPLC or GC-MS method are described in Vu Duc et al. (1995). IST has participated in PAH interlaboratory certifications of reference materials organised by EU-SMT (BCR 1997).

9.3.3 Sampling and determination of diisocyanates in foam

This experiment is of additional interest since the surface of the foam elements is coated with a chemical reagent. When the same pieces of foam are used for size selective sampling of the isocyanates droplets, an on-site derivatization occurs. The derivatized isocyanates are then desorbed by a solvent and analysed by HPLC with UV and/or EC (electrochemical) detection. The feasibility of such approach is clearly demonstrated.

Fig. 12 shows a HPLC-EC chromatographic profile of isocyanate derivative of HDI and prepolymer sampled on PU foam during painting operation with polyurethane based paint mixture.

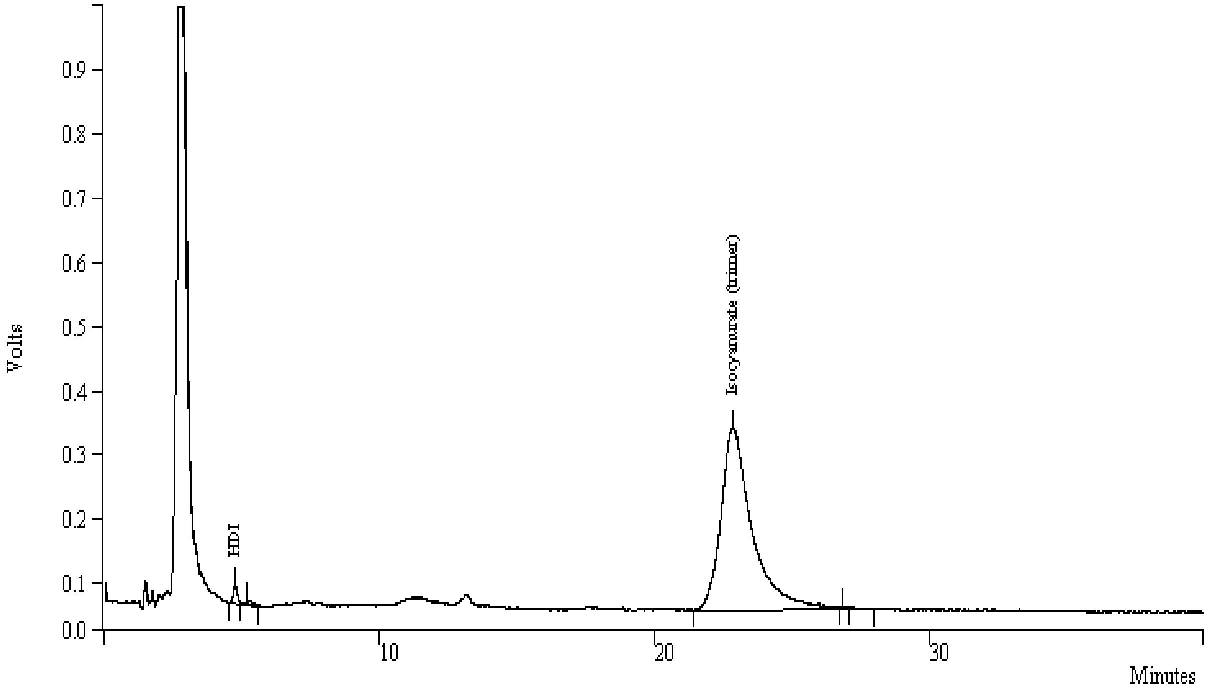

Figure 12: HPLC-EC chromatographic profile of isocyanate derivative of HDI and prepolymer sampled on PU foam during painting operation with polyurethane based paint mixture.

The standard method used at IST, “Sampling and analysis of monomer and prepolymers of isocyanates”, has been evaluated in EU SMT interlaboratory comparisons (TNO 1995). The procedure was also applied to TDI and MDI (respectively 2,4 and 2,6-toluene diisocyanates and 4,4'-methylenediphenyl diisocyanate) (Vu Duc et al. 1997, Huynh et al. 1992, Huynh et al. 1989).

10 Conclusions

After reviewing the former developments in use of porous foams for aerosol sampling, this EC research project concentrated on polyurethane foam (PUF) as this material is cheap, easily obtainable, most well characterised and has a track record of successful use in aerosol sampling. Different production sources of this material were checked. A description of the foam characteristics was improved and the cell diameter was found to be the most important measure. This assures a better exchange of data between manufacturers and appliers as well as better simulation capabilities for foam penetration characteristics.

The foam quality was found to be good for particulate aerosol sampling after applying a cleaning procedure to the foam to remove its particulate impurities of about 1 % of weight. In case of sampling organic compounds using foams, a more detailed cleaning procedure has to be applied. Significant amounts of extractable phthalate- and phosphate-type plasticisers can be found. The PUF appears to have a good chemical resistance to several classic organic solvents. Overall between 4 and 5% of weight can be removed by cleaning a 45 or 60 ppi foam.

The improved design model should enable the user to calculate the dimensions and grades of foam modules that will have a specified particle size-selective behaviour at a chosen flow rate. A large dataset of measurements of aerosol penetration through porous polyurethane foams was compared with predictions obtained using an existing published empirical model for polyurethane foam aerosol penetration. Once all errors in the implementation of the empirical model were eliminated, excellent agreement between measured and modelled values were obtained, despite the fact that the empirical model was extrapolated well beyond its original range of application. In general, the measured and modelled particle aerodynamic diameters corresponding to any given penetration value agreed to within 5%, which is within experimental error for the polyurethane foams.

The improved model was used to construct an Excel spreadsheet for designing foam modules for aerosol sampling applications. Different combinations of foam specifications can be used to make foam modules meeting the EN 481 aerosol sampling conventions. The spreadsheet predictions are compared with real penetration curves measured for some prototype foam modules already in use. The utility of the design model is mainly limited by the availability of supplies of foams with a precisely specified foam porosity (i.e. cell diameter), since this is the principle factor governing the aerosol penetration. Hence it is likely that prototype foam modules will need to be verified experimentally unless this supply problem can be solved.

On the basis of the semi-empirical model various plug geometries for the two size selective foam plugs were chosen to fit into the modified IOM and PGP-GSP inhalable samplers. Each two prototype personal air samplers (IOM and PGP based) were designed and manufactured for two-stage sampling (IOM-IT/IOM-IR and PGP IR/PGP-IT) and for three-stage sampling (IOM-ITR and PGP-ITR). They include one or two foam holders additionally to the plane filter (e.g. membrane) and increase the dimensions of the basic inhalable samplers, but are still light-weight and easy to carry. The laboratory tests and field trials showed the applicability and should give advice for improvements. The samplers shall especially be easy to handle during field measurements. Later improvements of the design, e.g. when being produced by manufacturers, will be taken into account. Potential manufacturers will be interested in producing and selling these new types of personal air samplers. Special attention must be paid on the quality control of the foams used in each stage, i.e. the cell diameter of each foam batch from production must be controlled before applying.

Based on the measurements of the particle penetration of modules, designs have been developed for all of the modules, other than PGP thoracic module, which are satisfactory in terms of their performance with respect to the appropriate size convention.

However, the PGP thoracic module results need to be interpreted with some caution (and to some extent, the IOM thoracic module results. The APS measurement had an effective upper limit of 15 µm and for many of the experiments there is a paucity of data in this size range and so these positive biases are derived from extrapolations of the penetration curve. In addition, the count statistics were very poor at all sizes above 12 µm. The bias map approach is very sensitive to the zero penetration point and very large positive biases can be produced.

Entire porous foam size selective aerosol samplers are able to sample the health-related aerosol fractions laid down by the international organisations for standardisation. (CEN 1993, ACGIH 1994-1995, ISO 1995). Sampling bias can be minimised by judicious choice of sampler in relation to the expected particle size distribution of the measured aerosol. The conventional sampling condition is fairly well satisfied in case of the PGP sampler, particularly in its thoracic version PGP-IT. In case of the PGP respirable sampler and the IOM sampler in both versions, the experimental sampling efficiency presents a slightly higher slope and higher d_{50} than expected. The design of both prototype samplers IOM-ITR, PGP-ITR does not allow for a further change of foam geometry or flow rate to improve their performance. A slight modification of foam porosity could be a way to enhance sampling efficiency but this depends on the foam manufacturers.

The handling operations for mounting the three-stage samplers are not difficult, as seen in field tests. But is has been found to have a possibility for changing the modules in the field which is sufficient clean in order to avoid contamination of the modules. As the lids for the modules were provisional, any improvement can be expected. Special boxes for transportation of the modules are seen as advantageous.

The stability of PU foam weight with suitable geometries is found to be at least as good as the used membrane filters out of mixed cellulose esters (e.g. cellulose nitrate) or glass fibres, derived with standard weighing environment. The limits of detection (LOD) of the thoracic and respirable foam plug will be ≤ 0.069 mg, the limit of quantitation (LOQ) ≤ 0.230 mg. These results were achieved in a laboratory room with changing humidity and can be decreased by a better control of temperature and humidity or even by using a glove box.

The time for a foam to reach equilibrium weight due to different humidity and temperature is less than 4 hours. A storage time of 12 hours in stable conditions will be sufficient before the weighing operation.

The weight dependence on humidity was found as 0.02 mg per 1 % change in relative humidity for the thoracic foam and 0.04 mg per 1 % change in relative humidity for the respirable foam. But this is only valid for the foam porosities and geometries chosen for the prototype foam modules of the PGP-ITR. When choosing different foam plug geometries, the weight dependence can be estimated. A coating with 10 % Vaseline in xylene for the thoracic foam did not change the humidity dependence.

The problem of particle fall-off at the thoracic foam could be minimised when coating the PU foam with a few weight percent of Vaseline (paraffins) in xylene. A reduction from 55 % to 7.4 % loss of dolomite dust load was measured, since this is an important problem for transportation. Field tests at different workplaces revealed a LOD of 0.15 mg and a LOQ of 0.5 mg. If new materials are to be chosen for the foam holders, others than aluminium, the variation of the whole foam cassette has to be determined again. In the field tests only holders out of aluminium were used.

The analysis of elements in the dust load of a foam was tested with used standard methods. the preparation of loaded foams using an acid digestion with a mixture of nitric acid/hydrochloric acid to decompose the foam matrix. From stable suspensions, fractions will be filtered before analytic determination by use of ICP mass spectrometry. At this stage, the polyurethane foams investigated can not be recommended for the chemical analysis of calcium and tin. The foam material itself contains higher blank values of Ca and Sn with especially high variations of Ca. The high variations of Ca can also be caused by manually washing the foams before sampling.
With suitable preparation of the foam material, it will be also possible to use the PUF for sampling organic compounds like polycyclic aromatic hydrocarbons (PAH) or diisocyanates.

A further qualification of this improved sampling method using porous foams is to be done in the future, parallel to its integration in national sampling systems for occupational exposure measurements. The first steps towards this aim are done.

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