

Sampling and chemical characterization of aerosols in workplace air

Siri Hetland and Yngvar Thomassen

National Institute of Occupational Health, P.O Box 8149 DEP, N-0033 Oslo 1, Norway.

Abstract

Contamination of the air in the workroom as well as the outside atmosphere is discussed. The particle type, composition and size distribution of aerosol contaminants is characteristic of a given type of work atmosphere. Health factors are discussed.

Sampling methods and the chemical composition of samples are discussed in relation to analytical methods. In particular AAS, flame and electrothermal methods are considered with respect to analysis of these samples.

The importance of reference materials and standards is stated.

SAMPLING FOR AEROSOLS IN WORKPLACE AIR

The inhalation of aerosols is a problem not only for industrial workers but also for the general population. Fractions of the airborne particulates are deposited in the respiratory tract and may give rise to undesirable effects. Since the complete removal of airborne environmental pollutants is impossible, concentration limits for contaminants have been established for a variety of workplaces (threshold limit values (TLV's)) in an attempt at preventing adverse health effects.

The application of modern physical methods in analytical chemistry makes it possible to identify the origin and source of organic and inorganic particulate air pollutants. Some of the most important factors used in the characterization of airborne particulates are size, shape, optical and electrical properties, structure, heterogeneity and chemical composition. The particle type, chemical composition and size distribution of aerosol contaminants are usually quite characteristic for a given type of work atmosphere and affect the deposition of different chemical species in the lung. Total amounts of contaminating particles and droplets are of interest whenever these may cause adverse effects either at or close to deposition sites in the extrathoracic region (i.e. the head), or systemically after deposition of soluble materials anywhere in the respiratory tract.

The necessity for the speciation of elements in aerosol mass fractions has also stimulated interest in the design of new aerosol samplers, incorporating characteristics which correspond to the inspirability of particulate by humans, for industrial hygiene applications. A number of personal samplers for "total" aerosol have been developed. The Institute of Occupational Medicine (IOM) in Edinburgh, Scotland, constructed the first device specifically for sampling total aerosols according to the inspirability criterion⁽¹⁾. Several samplers have been evaluated, and the best results were given by the IOM sampler⁽²⁾. The American 37 mm plastic cassette personal sampler, widely used by occupational hygienists not only in the US but also in the Nordic countries, produces results in fair agreement with the inspirability curve⁽³⁾. However, the performance test results show a decrease in sampling efficiency with an increase in particle size. In recent years a 25 mm diameter plastic cassette for aerosol sampling in the US has also been introduced. Since little has yet been done to test the performance of this device and in view of its wide use in Norway, we have compared the sampling efficiency of the 25 mm cassette with the IOM sampler.

The two types of aerosol samplers were mounted to the left and right of the breathing zone of six workers who are involved in the production of lead batteries and are thus exposed to lead-containing dust. During the lunch break the positions of the two samplers was changed in order to minimize any effect of systematic local inhomogeneity in the work atmosphere. The flow rate was 2.0 l/min for both samplers during the 8 hours of sampling. The total amount of inspirable dust was measured gravimetrically and the lead collected on the filters was measured by flame atomic absorption spectrometry after nitric acid digestion of the filters.

The amount of lead in particles dislodged from the filter during normal handling was estimated by washing the inner surfaces of the samplers with a 0.5% Triton X-100 aqueous solution. The lead content of this solution was measured by electrothermal atomic absorption spectrometry after nitric acid digestion. The average amount of lead found on the internal walls of the cassette, expressed in % of total aspirated lead, was 10 (sd=10, range 1-33) and 14 (sd=13, range 1-39) for the IOM and 25mm samplers, respectively. This shows that losses on the internal cassette surfaces may be a major source of error in measurements of aerosol contaminants if this sample fraction is neglected.

The results in Table 1 show overall differences between the two types of samplers and especially for samples 1 - 4. In this particular working area represented by these samples, the dust originated from lead oxides of large particle size. All other samples were obtained in areas where lead is most likely to be present as fumes. The samples were tested for statistical significant differences by use of Wilcoxon's matched pair-test (Table 2). Although the number of samples is small, it is reasonable to conclude that the 25mm sampler underestimates total inspirable dust in general.

It also seems clear, though not statistically significant, that the amount of lead collected on 25 mm sampler is lower. Much work must yet be done to properly evaluate the aspiration efficiencies of the personal samplers used in different countries. Since it is almost impossible to simulate true practical conditions in the laboratory, the ultimate test of sampler performance in given practical applications involves assessment in field trials. There is an urgent need for standardization of the sampling equipment used for workplace air monitoring.

Table 1 *Sampling efficiency of inspirable dust and lead in % for the American Model 25 mm plastic filter cassette compared with the IOM sampler (IOM=100%)*

Sample	Efficiency		Sample	Efficiency	
	Insp. dust	Lead*		Insp. dust	Lead*
1	74	56	7	78	112
2	20	47	8	31	40
3	25	44	9	95	83
4	51	65	10	52	78
5	79	70	11	60	123
6	148	222			

* Lead on internal surfaces of the cassette was included

Table 2 *Concentrations of inspirable dust and lead in air during production of lead batteries*

	Number of samples	Median in mg/m ³		p-value
		IOM	25 mm	
Inspirable dust	11	0.78	0.33	0.01
Lead*	11	0.176	0.143	0.06

* Lead on internal surfaces of the cassette was included

MEASUREMENT OF ELEMENTS IN AEROSOLS

The chemical characterization of the workplace atmosphere containing a variety of elements, often in specific chemical forms, requires sampling and analytical techniques which are capable of determining a broad concentration range of many elements in various matrices. Up to now flame atomic absorption spectrometry has dominated the field of the sequential measurement of elements in solution. However, flames have the limitation of relatively low temperatures, making the measurement of refractory elements or of elements with high excitation energies very difficult. With the higher temperatures of the Inductively Coupled Argon Plasma (ICP) source compared to flames, the larger linear concentration range, greatly reduced inter-element interferences and multi-element capabilities, ICP-atomic emission spectrometry is an excellent technique for the analysis of the workroom environment. The occurrence of spectral interferences is common in ICP-AES and the selection of appropriate analytical lines may require some compromise between detecting power and spectral interferences from major concomitants. In our laboratory we have successfully applied ICP-AES for a decade in the chemical characterization of workplace aerosols. Using the spectral conditions listed in Table 3 the only interferences seriously affecting measurements are copper on phosphorous and aluminium on lead, assuming that the airborne concentrations do not exceed the TLV's more than 10 times.

Table 3 Spectral conditions in the chemical characterization of workplace aerosols by ICP-AES

Analytical line nm	Spectral interference	Concentration in calibrating solution in µg/ml
Al(I) 396.152	Ca (∕), BC-0.09 nm	10
As(I) 189.042		5
Ba(II) 455.403		10
Be(I) 249.473		1
Ca(II) 393.366		10
Cd(II) 214.438		1
Co(II) 228.616		2
Cr(II) 205.552	Fe (^), BC+0.07 nm	10
Cu(I) 324.754		25
Fe(II) 259.940		100
Hg(II) 194.227		1
Mg(II) 279.553		10
Mn(II) 257.610		20
Mo(II) 202.030	Fe (∕), BC+0.13 nm	2
Nb(II) 212.654		5
Ni(II) 231.604		5
P(I) 214.914	Cu (^)	10
Pb(II) 220.353	Cu (-), Ni (-), Al (∕), BC-0.07 nm	5
Sb(II) 206.833		5
Si(I) 251.611		10
Sn(II) 189.980		1
Ta(II) 223.948	Cu (∖), Ni (-), BC + 0.06 nm	5
Ti(II) 307.864		5
V(II) 310.230		1
W(II) 207.911	Al (-), Zn (^) BC - 0.07 nm	1
Y(II) 371.030		2
Zn(II) 206.200		25
Zr(II) 343.823		1

(-) indicates simple background shift

(∖), (∕) indicates sloping background shift

(^) indicates direct spectral overlap

BC spectral region for appropriate background correction

Table 4 *Analytical methods used for measurements of elements in simulated workplace air filters*

Method	Code	Number of laboratories
Electrothermal atomic absorption spectrometry	EAAS	2
Inductively coupled plasma atomic emission spectrometry	ICP-AES	4
Inductively coupled plasma mass spectrometry	ICP-MS	1
Flame atomic absorption spectrometry	FAAS	10
Cold-vapour atomic absorption spectrometry	CVAAS	2
Energy-dispersive X-ray fluorescence	XRF	1

It should be recognized that extreme care must be exercised in avoiding incompatible element combinations in multi-element standard solutions which could give rise to precipitation. In order to obtain optimum multi-elemental dissolution of workplace particulates, a pressure decomposition of filters in a teflon autoclave with 1.5 ml aqua regia and 0.5 ml hydrofluoric acid is recommended.

Inter-laboratory comparisons of both real workplace air filters and filters from a simulated welding atmosphere have revealed, not surprisingly, differences in results among laboratories⁽⁴⁾. The accuracy of a measurement is not readily determined and generally involves the analysis of reference materials or the comparison of results obtained by independent methods. Reference materials which approximate the matrix composition and analyte concentration ranges of interest are not presently available.

The National Institute of Occupational Health is actively working on the development of such materials for quality assurance programs. Thirty-seven mm cellulose acetate filters were spiked with an aqueous solution simulating welding fumes and containing concentrations of selected elements corresponding to current threshold limit values of contaminants in workplace air. The filter to filter consistency was assured by identical treatment in all production steps and the homogeneity of the filter material throughout production was typically 1-2% (RSD) for most elements.

A cooperative study among 13 Norwegian and Swedish laboratories was conducted to measure the mass of a variety of elements in these simulated workplace air filters. No constraints were imposed on the analytical method to be used. The numbers of laboratories using various analytical methods are listed in Table 4. Each participant received two filters each from two different production batches. In Tables 5 and 6 are assembled the individual mean values reported for each element, along with the overall mean calculated after removal of outliers. Each laboratory and method have been given equal weight in the calculation of mean concentrations and uncertainties. It is to be hoped that this material may help to fill the gap between the availability of and the need for reference materials for quality assurance of the measurement of elements in workplace air.

Acknowledgement

Workers and management at Tudor-Sønnak Ltd., plant in Horten, Norway made the comparison of samplers in real exposure situations possible.

Table 5 Analytical results and recommended values of constituent elements in Batch A-1. The values in parentheses are information values only

Element	FAAS µg	ETAAS µg	CVAAS µg	ICP-AES µg	ICP-MS µg	XRF µg	Recommended value µg±SD
Aluminium	80, 90, 78, 84, 93			79, 101	79		86±8
Antimony		15		20	15		17±3
Arsenic		2.6, 4.0			2.9		(3.2±0.7)
Barium	153			155, 148, 149	135		148±8
Beryllium				0.7, 0.8	0.8		0.8±0.1
Boron				198, 192, 210, 191	205		200±8
Cadmium	14, 14, 14, 13, 13 14, 15			14, 16, 16, 12	14		14±1
Calcium	85, 80, 80, 94			85, 99			87±8
Chromium	203, 187, 180, 201, 178, 182, 193, 173, 178			169, 192, 191	166	191	185±11
Cobalt	36, 32, 37, 36, 33, 34			33, 41, 37	33	33	35±3
Copper	698, 679, 695, 668, 659, 702, 672, 640, 703			650, 705	641	697	678±24
Iron	704, 671, 585, 675, 682, 580, 669, 603, 655			594, 792, 692		601	654±61
Lead	34, 35, 30, 33, 32, 32, 36			29, 38	30	30	33±3
Magnesium	59, 50, 55, 52, 65			51, 54	59		56±5
Manganese	359, 323, 370, 359, 363, 334, 341, 344, 351, 359			325, 347	327	377	349±17
Mercury			8.2, 10	10			9.4±1
Molybdenum	23			24, 23	23	21	23±1
Nickel	84, 84, 84, 82, 88, 75, 77, 79			78, 88, 80	82	85	82±4
Vanadium	15, 16			12, 14	12		14±2
Zinc	336, 320, 300, 320, 337, 316 328			304, 348, 317	298		320±16

Table 6 Analytical results and recommended values of constituent elements in Batch B-1

Element	FAAS µg	ETAAS µg	CVAAS µg	ICP-AES µg	ICP-MS µg	XRF µg	Recommended value µg±SD
Aluminium	53, 60, 55, 49, 61				58, 58	55	56±4
Antimony		6.3			7.8		7.1±1.1
Arsenic		1.8, 2.3			2.3		2.1±0.2
Barium	74, 66			68, 74, 71			71±4
Beryllium				0.4, 0.4	0.3		0.4±0.1
Boron				90, 87, 91, 77	85		86±6
Barium	9, 9, 10, 8, 8, 9, 9, 10, 9			8, 9, 8, 9	8		9±1
Calcium	97, 84, 100			100, 106			97±8
Chromium	100, 92, 98, 90, 94, 93, 94, 93, 94			91, 93, 86	92		93±3
Cobalt	22, 18, 22, 22, 18, 23			21, 22, 21	20	23	21±2
Copper	382, 375, 375, 400, 362, 358, 366, 372			372, 413, 354	356		374±18
Iron	668, 647, 520, 625, 631, 615, 620, 602, 579			598, 584	567	610	605±38
Lead	26, 25, 22, 23, 25, 24, 24, 25			22	25	26	24±1
Magnesium	41, 38, 41, 36, 44			40, 39	43		40±3
Manganese	222, 240, 217, 216, 240, 212, 214, 213, 196, 209			217, 217, 201	212		216±12
Mercury			6.5, 8.0	5.9			6.8±1.1
Molybdenum	18			20, 18	19	19	19±1
Nickel	48, 49, 52, 46, 51, 47, 45, 47, 49			49, 49, 47	55	55	49±3
Vanadium	9			6, 7	7	6	7±1
Zinc	176, 170, 168, 170, 168, 160, 178, 169			173, 180, 161	163		170±6

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