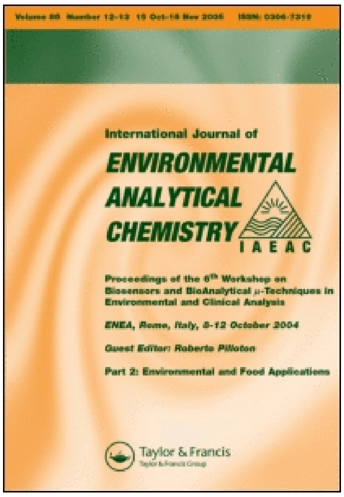

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C. Segebade[a]; B. F. Schmitt[a]; M. Kühl[a]
[a] Bundesanstalt für Materialprüfung (BAM), Berlin, Germany

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Instrumental Analysis of Air Dust by Activation with Photons and Photoneutrons

C. SEGEBADE, B. F. SCHMITT and M. KÜHL†

Bundesanstalt für Materialprüfung (BAM), Berlin, Germany

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Twelve Elements (Ca, Cr, Mn, Co, Ni, Zn, As, Br, Cd, Sn, Sb, Pb) in airborne particulate samples were analysed with help of an electron linear accelerator. Analyses were carried out instrumentally. The air dust filters were pressed to pellets and irradiated for approximately five hours. Eleven of the named elements were activated with high energy bremsstrahlung and one (Mn) with photoneutrons. Samples were taken over a one year's period (spring 1981 to spring 1982) in different types of location (rural and urban, residential and industrial) within the Federal Republic of Germany.

Another series of analyses has been performed during this year (1984). Air dust samples have been taken from twenty different locations in the city of West Berlin. These samples were analysed for the above listed set of elements plus several additional ones, namely Cl, Fe, Se, Mo, Tl and U by photonuclear activation, and V by activation with photoneutrons.

Particular attention has been directed to the filter material. The contamination levels in different materials (glass fibre, polycarbonate, cellulose acetate) were examined as well as their behaviour during long-time radiation exposure.

KEY WORDS: Air dust, activation analysis.

THE INVESTIGATION PROGRAMME

In March 1981, the systematic study of seventeen elements of environmental interest in airborne particulate was initiated within

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the Coordinated Air Dust Programme (LVPr) of the Federal Radiation Technology Working Group (AFR).

The sampling was carried out under comparable conditions at five selected locations within the Federal Republic using specially developed large filter high volume samplers. Cellulose acetate membrane filters were found most suitable with respect to the contamination level by the elements of interest, processability and behaviour during analysis (e.g. radiation exposure) as well.

The sampling locations were: Hamburg, Mannheim, Karlsruhe, München and Deuselbach. The latter served as "clean air" reference. Seven-days samples were collected including various interruptions so as to obtain an average dust load of about 0.5 mg/cm^2.

The following elements were analysed: S, Ca, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Br, Cd, Sn, Sb, Hg, Pb, among these by activation with photons and photoneutrons: Ca, Cr, Mn, Co, Ni, Zn, As, Br, Cd, Sn, Sb and Pb.

Twelve laboratories using eight different analytical methods participated in this programme. Thereby a high degree of reliability of the analytical results could be confirmed, based upon more than 30,000 single values.

A detailed description of the programme can be found in Ref. 1.

A separate air dust investigation programme covering the city area of West Berlin was started in the beginning of 1984. Airborne particulate samples have been collected at twenty different locations including those with light or heavy traffic activity, industrialised and forest regions. Polycarbonate filters have been used for aerosol sampling. In this programme, Cl, Ca, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Mo, Cd, Sn, Sb, Tl, Pb and U have been analysed, among them V and Mn by activation with photoneutrons. Since this programme is not yet finalised, no reference can be given at this point.

THE ANALYSIS METHOD

Activation

The basic principle of activation analysis with high energy photons has been described in detail elsewhere[2,3,4] and therefore will be discussed only briefly here.

With the help of the electron linear accelerator of the Bundesanstalt für Materialprüfung (BAM LINAC) electrons can be accelerated to a maximum energy of 35 MeV; for photon activation analysis usually 30 MeV, in some cases a bit less than 20 MeV have been selected. The electrons are then absorbed in a water-cooled tantalum bremsstrahlung converter target (see Figures 1 and 2). The total thickness of the target is seven millimeters so as to absorb and

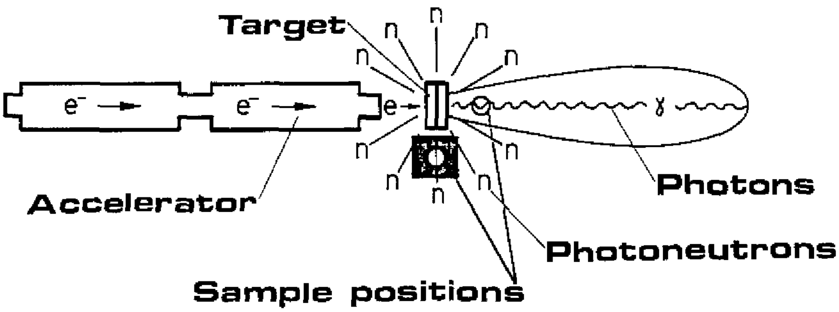

FIGURE 1 Irradiation positions at the BAM LINAC.

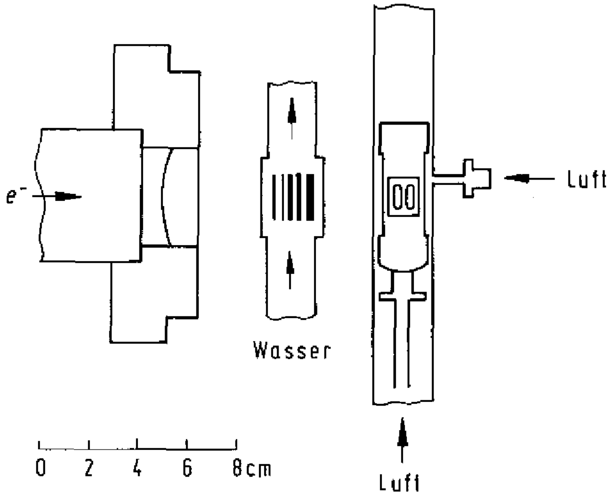

FIGURE 2 Photon irradiation position and compressed air transport terminal at the BAM LINAC.

convert all electrons. When the electrons are decelerated in the coulomb field of the target nuclei, about one-half of their energy is converted to bremsstrahlung which is radiated in the foreward direction. The photon radiation energy is continuous with a maximum which equals the electron energy. It is concentrated in a narrow cone with an apical angle of a few degrees. The sample to be irradiated is positioned directly behind the target as close as convenient, normally about 5 cm. Generally the samples are transported to and returned from the irradiation position packed in an aluminium container through a pneumatic tube sample transfer system (see Figure 2).

The most sensitive photonuclear reaction for activation analysis is of the (γ, n)-type. The threshold energy (i.e. the minimum energy to induce a reaction) for this reaction smoothly decreases with increasing atomic number of the target nucleus. It varies from about 19 MeV for carbon to 6 MeV for uranium. The energy of maximum cross section ("giant resonance") is about 6 to 9 MeV higher than the threshold energy. The value of this maximum rises with the atomic number and is about 0.01 barn for carbon and about 0.7 barn for uranium.

The location of the highest photon flux density is within the bremsstrahlung converter. Therefore, by the photonuclear reaction

$$^{181}\mathrm{Ta}(\gamma, n)^{180,\,180m}\mathrm{Ta}$$

which is induced to the converter material, an intense photoneutron radiation is produced which—unlike bremsstrahlung radiation—is isotropical (see Figure 1); the energy distribution of the neutrons is similar to that of fission neutrons.[5,6] By proper selection of the irradiation position one can exploit this neutron flux for activation with negligible photon contamination (see Figures 1 and 3). In the present work, vanadium and manganese were analysed by activation with photoneutrons since the photonuclear data of these elements are quite unfavourable for analysis.

Radiation Spectroscopy

Both gamma—ray and low energy photon spectrometry have been applied for product activity measurement using large volume coaxial

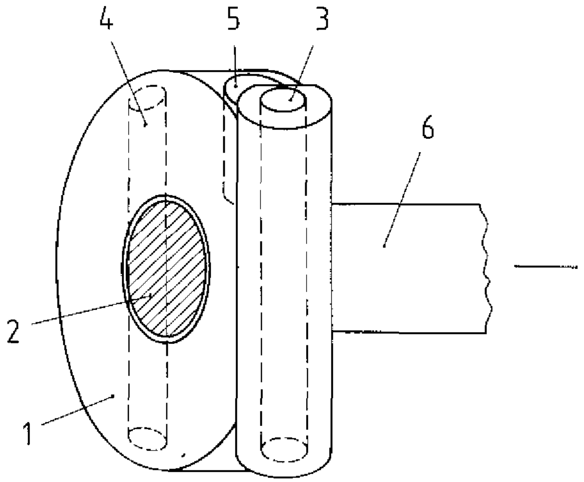

FIGURE 3 Photoneutron moderator at the BAM LINAC. 1—Moderator annulus. 2—Tantalum bremsstrahlung converter. 3—Thermal neutron terminal (Cd—ratio is about 20). 4—Fast neutron terminal (Cd—ratio is about 1). 5—Irradiation position for large volume samples (about 100 ml). 6—Accelerator tube.

and small planar germanium diodes, respectively. Low energy photon spectrometry (LEPS) is particularly useful for photon activation analysis since primarily neutron deficient nuclei are produced during bremsstrahlung exposure. Neutron deficient nuclei of medium to high atomic number predominantly decay by electron capture whereby an intense characteristic X—radiation is emitted which can be favourably measured by LEPS. More details about the use of LEPS in photon activation analysis can be found in Refs. 7, 8, 9.

EXPERIMENTAL

Sample preparation and irradiation

The air particulate filters were impregnated with an internal monitor solution. Scandium and samarium were used as additive internal standards. The use of internal standards in photon activation analysis is described extensively elsewhere.[10] The filters were then dried at 105°C and pressed to pellets of 13 mm diameter and less than one millimeter thickness so as to avoid matrix absorption of soft photons during LEPS. After a first irradiation of 45 minutes with 20 MeV bremsstrahlung and a cooling period of about 1.5 hours, short-lived activities were measured (see Table I). 20 MeV electron energy was selected to suppress the activation of the matrix carbon by

$$^{12}\mathrm{C}(\gamma,n)^{11}\mathrm{C} \qquad T=20\,\mathrm{min}$$

which has a threshold energy of about 20 MeV. For internal radiation dose monitoring

$$^{45}\mathrm{Sc}(\gamma,n)^{44}\mathrm{Sc} \quad \begin{array}{l} T=3.92\,\mathrm{h} \\ E=1157\,\mathrm{keV} \end{array}$$

was used.

After one day the samples were re-activated for five hours at 30 MeV electron energy; the mean electron beam current was 150 microamperes. The long-lived activation products ($T>10$ hours) were measured after a decay period of two days (see Table I). The reaction of the internal standard

$$^{45}\mathrm{Sc}(\gamma,n)^{44m}\mathrm{Sc} \qquad \begin{array}{l} T=2.44\,\mathrm{d} \\ E=1157\,\mathrm{keV} \end{array}$$

was used for internal radiation flux monitoring. Another batch of samples was irradiated simultaneously in the "fast" neutron position (see Figures 1 and 3). This position allows photoneutron irradiation at the closest possible distance to the radiation source. The neutron flux density in this position is several $10^{10}\,\mathrm{cm}^{-2}\mathrm{s}^{-1}$ with a cadmium ratio of about 1. By several reasons no internal standard but an external neutron flux monitor (copper disc) was used this time. After about five minutes decay time the activity of ^{52}V and after another decay period of about 0.5 hours ^{56}Mn were measured (see Table I).

Photon spectrometry

The soft photon emission of the product radionuclides ($E \leqq 190$ keV; characteristic X-rays and soft gamma-rays) was measured with planar intrinsic high purity germanium diodes (see Table I). The

TABLE I

Nuclear reactions and data of the analysed elements.

Element	Reaction	T	E in keV(I%)
Cl	$^{35}\mathrm{Cl}(\gamma,n)^{34m}\mathrm{Cl}$	32 m	146(36) 2129(48)
Ca	$^{44}\mathrm{Ca}(\gamma,p)^{43}\mathrm{K}$	22.2 h	372(100) 593(13) 616(87)
	$^{48}\mathrm{Ca}(\gamma,n)^{47}\mathrm{Ca}$	4.54 d	1297(75)
V	$^{51}\mathrm{V}(n,\gamma)^{52}\mathrm{V}$[a]	3.75 m	1434(100)
Cr	$^{52}\mathrm{Cr}(\gamma,n)^{51}\mathrm{Cr}$	27.7 d	320(10)
Mn	$^{55}\mathrm{Mn}(n,\gamma)^{56}\mathrm{Mn}$[a]	2.58 h	847(99) 1811(30)
Fe	$^{57}\mathrm{Fe}(\gamma,p)^{56}\mathrm{Mn}$	2.58 h	847(99) 1811(30)
Co	$^{59}\mathrm{Co}(\gamma,n)^{58}\mathrm{Co}$	71.3 d	811(99)
Ni	$^{58}\mathrm{Ni}(\gamma,n)^{57}\mathrm{Ni}$	36 h	1378(85) 1920(10)
Zn	$^{68}\mathrm{Zn}(\gamma,p)^{67}\mathrm{Cu}$	62 h	93(16)[b] 185(45)[b]
As	$^{75}\mathrm{As}(\gamma,n)^{74}\mathrm{As}$	17.8 d	595(60)
Se	$^{76}\mathrm{Se}(\gamma,n)^{75}\mathrm{Se}$	120 d	136(58)[b]
Br	$^{79}\mathrm{Br}(\gamma,2n)^{77}\mathrm{Br}$	56 h	239(26)
Mo	$^{100}\mathrm{Mo}(\gamma,n)^{99}\mathrm{Mo}$	66 h	
	$^{99}\mathrm{Mo}\rightarrow{}^{99m}\mathrm{Tc}$	66 h	141(85)[b]
Cd	$^{116}\mathrm{Cd}(\gamma,n)^{115}\mathrm{Cd}$	53.4 h	
	$^{115}\mathrm{Cd}\rightarrow{}^{115m}\mathrm{In}$	53.4 h	336(45)
Sn	$^{112}\mathrm{Sn}(\gamma,p)^{111}\mathrm{In}$	2.83 d	171(91)[b] 245(94)
Sb	$^{123}\mathrm{Sb}(\gamma,n)^{122}\mathrm{Sb}$	2.7 d	564(63)
Tl	$^{203}\mathrm{Tl}(\gamma,n)^{202}\mathrm{Tl}$	12.2 d	440(95)
Pb	$^{204}\mathrm{Pb}(\gamma,n)^{203}\mathrm{Pb}$	52.1 h	73(47)[b] 279(81)
U	$^{238}\mathrm{U}(\gamma,n)^{237}\mathrm{U}$	6.75 d	59.53(35)[b] 208(23)

[a] Activated with photoneutrons.

[b] *Also or exclusively measured with LEPS.*

higher gamma-ray energies ($E > 120\,\mathrm{keV}$) were measured with standard lithium-drifted germanium detectors. The physical data of these detectors can be taken out of Refs. 7, 8, 9. In the quantitative evaluation of the low energy photon spectra, the internal monitor reaction

$$^{154}\mathrm{Sm}(\gamma, n)^{153}\mathrm{Sm} \qquad \begin{array}{l} T = 46.75\,\mathrm{h} \\ E = 103\,\mathrm{keV} \end{array}$$

was used for photon flux monitoring. Spectra were stored in 8K-pulse height analysers using 2048 channels for each spectrum and then processed by computer.

SOURCES OF ERROR

Many possible sources of error were excluded by the use of internal standards.[10] The data given in Table II represent the analysis results of nickel in a candidate multielement reference material obtained by conventional calculation on the sample mass basis and by calculation with internal standard normalisation in comparison to values obtained by other methods. These data clearly indicate the superiority of the internal monitor technique with respect to the precision

TABLE II

Comparison of results of nickel analyses in waste incineration fly ash, evaluated on mass- and internal standard basis; no standard deviation can be given for the comparative mean value of the other methods since the single data have largely different precisions. The values are given in μg/g.

Photon Activation Analysis		
Mass basis	Internal standard	Other methods
130	129	128±5 (RFA)
117	120	123±15(NAA)
126	122	134±5 (AAS)
98	133	126±5 (RFA)
107	125	
X: 118±13	126±5	128

and—if the mean value obtained by the other methods can serve as a comparison reference—the accuracy of the concentration data.

Errors due to contamination are less probable as compared to non-activation methods since contamination after bremsstrahlung exposure has no influence upon the measured signal. Contamination occurring before activation was accounted for by running frequent blanks.

The most relevant sources of error are nuclear interferences.[11,12,13] Competing reactions

$$^{55}\mathrm{Mn}(\gamma,n)^{54}\mathrm{Mn}$$
$$^{56}\mathrm{Fe}(\gamma,np)^{54}\mathrm{Mn}$$

as well as gamma-ray overlap

$$^{75}\mathrm{As}(\gamma,n)^{74}\mathrm{As} \qquad E=595\,\mathrm{keV}$$
$$^{44}\mathrm{Ca}(\gamma,p)^{43}\mathrm{K} \qquad E=593\,\mathrm{keV}$$

might occur. In favourable cases, the competing reaction in the upper case can be ruled out by selection of a lower activation energy as touched on above. The second type of interference can be circumvented in the case of largely different half-lives of the participating radionuclides (which is the case in the given example; $T=17.77\,\mathrm{d}$ and $22.2\,\mathrm{h}$, respectively). After a common measurement of both the short-lived nuclide is allowed to decay to negligible activity before a replicate measurement is performed. However, both ways of interference management are not practical in the case of many samples to be analysed, if a restricted time-schedule has to be kept. Therefore, the interferences given in Table III are accounted for by correction routines included in the computer programmes used for quantitative analysis evaluation,[13] taking into account a certain loss of the data quality.

During practical work it was stated that the analysis of cobalt is severely hampered by strong overlap interference of the 811 keV-line by $^{47}\mathrm{Ca}$ (808 keV) produced by $^{48}\mathrm{Ca}(\gamma,n)$. Since calcium is one of the major air dust components—whereas cobalt is present in comparably very small traces—the cobalt signal frequently suffered from severe loss of significance, hence another method of analysis is the method of choice in these cases, e.g. activation analysis with thermalised pile neutrons.

TABLE III

Interferences in photon activation analysis of air dust particulate

Element	Reaction	E in keV	Interference	E in keV
Cl[a]	$^{35}\mathrm{Cl}(\gamma,n)^{34m}\mathrm{Cl}$	2128	$^{39}\mathrm{K}(\gamma,\alpha n)^{34m}\mathrm{Cl}$	2128
Cr[a]	$^{52}\mathrm{Cr}(\gamma,n)^{51}\mathrm{Cr}$	320	$^{56}\mathrm{Fe}(\gamma,\alpha n)^{51}\mathrm{Cr}$	320
Mn[b]	$^{55}\mathrm{Mn}(\gamma,n)^{54}\mathrm{Mn}$	835	$^{56}\mathrm{Fe}(\gamma,np)^{54}\mathrm{Mn}$	835
Co	$^{59}\mathrm{Co}(\gamma,n)^{58}\mathrm{Co}$	811	$^{48}\mathrm{Ca}(\gamma,n)^{47}\mathrm{Ca}$	808
As	$^{75}\mathrm{As}(\gamma,n)^{74}\mathrm{As}$	595	$^{44}\mathrm{Ca}(\gamma,p)^{43}\mathrm{K}$	593
Tl	$^{203}\mathrm{Tl}(\gamma,n)^{202}\mathrm{Tl}$	440	$^{70}\mathrm{Zn}(\gamma,n)^{69m}\mathrm{Zn}$	439

[a] The interference can be neglected in the most cases; the interfering reaction has an extremely small activation cross section, so that it becomes significant only at very low concentrations of chlorine or chromium, respectively.

[b] After initial attempts to use the above given reaction the interference was later avoided by the use of activation with photoneutrons (see Table I).

As touched on above, the analysis of manganese suffers from strong interference by the competing iron reaction. Here again, iron as the source of interference is present in comparably high concentration levels. Therefore manganese was analysed by activation with photoneutrons (see Table I).

THE FILTER MATERIAL

Three different filter materials were examined, namely glass fibre, cellulose acetate and polycarbonate.

Glass fibre is durable against heat and radiation, but its composition and contamination level made it unacceptable for the present work. Large concentrations—partly more than one per cent of Mn, Fe, Zn, As and many other elements of environmental interest were detected in the filter matrix. Moreover, several major components (Na, Mg, Ca) produced a huge matrix background so that signals from say one milligram of dust layer were degraded by poor signal-to-Compton ratio, particularly in the lower energy region of the resulting gamma-ray spectrum.

Cellulose acetate was found suitable for the given task. It showed an extremely low contamination level and the background activity due to the matrix material did not exceed 20 minutes in half-life (^{11}C from matrix carbon). The material survived five-hours irradiations under the above described standard conditions fairly well. The material is easily soluble in acetone and many other solvents. Therefore it can be processed conveniently if required by the analysis procedure applied. A disadvantage is the sensitivity of the material against excessive humidity; special aerosol samplers must be available to prevent damage of the filters by any atmospheric precipitate activity.

Polycarbonate filters showed higher but still acceptable contamination level, particularly of Cl, Ca, Fe and Ni. The material is fairly soluble in several organic solvents but tended to be deformed under radiation bombardment, presumably through development of carbon dioxide. However, this material is insensitive against humidity attack and therefore could be used in the present work as well.

REFERENCE MATERIAL

Fly ash of a waste incineration facility in Berlin was used as a multielement reference material. Both industrial and private household waste have been incinerated in this station, and therefore the ash is enriched with elements which are of interest in the air dust analysis. Two batches of fly ash were prepared, one of them (which was used for this work) for use in our laboratory, the other one as candidate reference material to pass the certification procedure within the reference material programme of the European Community Reference Bureau (BCR). The overall composition is somewhat similar to that of an "average" urban air dust; high concentrations of Si, Ca, Cr, Fe, Cu, Zn and Pb (see Table IV; the values given for URM2 are not the final consensus concentrations but obtained in our laboratory exclusively; the BCR certification procedure is not yet completed) are present. Particularly URM1 has been used in our laboratory successfully in many analysis tasks and there is no reference material of similar composition commercially available hitherto. More details about production and use of this material can be found in Refs. 14, 15, 16.

COMPARISON OF THE RESULTS

Thermal neutron activation analysis, energy- and wavelength-dispersive X-ray fluorescence analysis, total reflection X-ray flu-

TABLE IV

Element contents of the waste incineration fly ash batches URM 1 and URM 2; given in μg/g or as indicated

Element	URM 1	URM 2	Element	URM 1	URM 2
C %	2.5	1.77	Y	34	27
F %	0.15	—	Zr	152	140
Na %	1.65	4.30	Nb	15.9	28
Mg %	1.80	2.18	Mo	24	—
Al %	8.28	10.16	Ag	42	65
Si %	14.00	14.04	Cd	250	474
S %	5.80	4.46	In	—	2.4
P %	0.3	0.55	Sn %	0.324	0.62
Cl %	1.28	4.21	Sb	220	417
K %	2.3	4.5	I	24	—
Ca %	10.16	8.80	Cs	16	14.7
Sc	20	4.1	Ba %	0.441	0.43
Ti %	0.71	0.85	La	34	25
V	117	47	Ce	56	43.4
Cr	410	832	Nd	44	—
Mn %	0.102	0.14	Sm	6	4.3
Fe %	7.89	2.20	Eu	0.23	0.44
Co	38	32	Tb	0.59	—
Ni	126	120	Yb	1.6	—
Cu	769	1305	Lu	0.6	0.4
Zn %	1.30	2.574	Hf	3.6	3.4
Ga	261	28	Ta	1.85	4.52
Ge	16.4	0.4	W	36	30
As	93	88	Au	0.6	1
Se	22	39	Hg	0.27	30.7
Br	136	293	Tl	3.9	3.1
Rb	139	110	Pb %	0.635	1.098
Sr	778	43	Th	11.3	11.2
			U	4.2	—

orescence analysis, flame- and flameless atomic absorption spectrometry, atomic emission spectroscopy with inductively coupled plasma, proton induced X-ray emission spectrometry, wet chemistry as well as instrumental photon activation analyses were applied by twelve laboratories during the intercomparison study. The complete list of all results obtained can be found in Ref. 1. The concentration data of three elements (Zn, Sb, Pb) obtained by photon activation analysis are represented in Figs. 4, 5, 6. In these diagrams, the photon activation values are compared with the mean values of all methods applied in the study. The obvious outliers will not be discussed here. Too high photon activation values possibly are due to contamination of yet unknown source. However, since no systematics can be recognised in the outlying values, their interpretation is not meaningful, whatsoever.

Generally the data agree fairly well. In several cases the precision of the photon activation results (it is not represented in the diagrams for their clearness' sake) is insufficient. The agreement of the values close to the determination limit is poor, particularly, of course, if the mean value of all methods is poorly precise (e.g. in the case of cadmium; see Ref. 1).

The average of all results assumed as "true" value, the concentrations of zinc and lead as obtained by photon activation seem

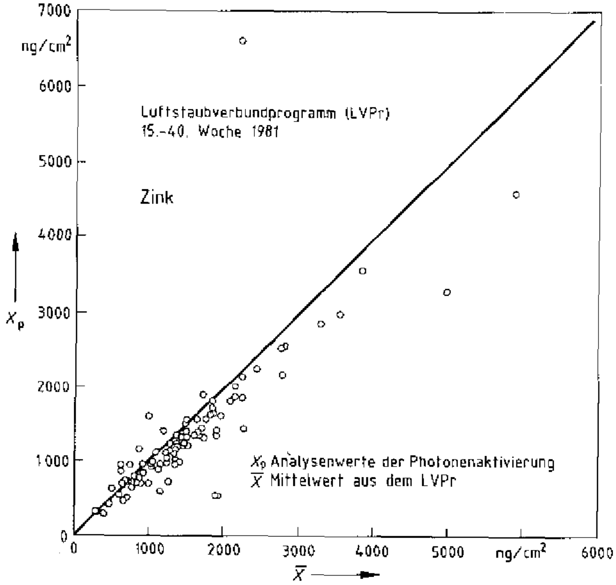

FIGURE 4 Comparison of zinc concentrations (photon activation versus average of all methods used).

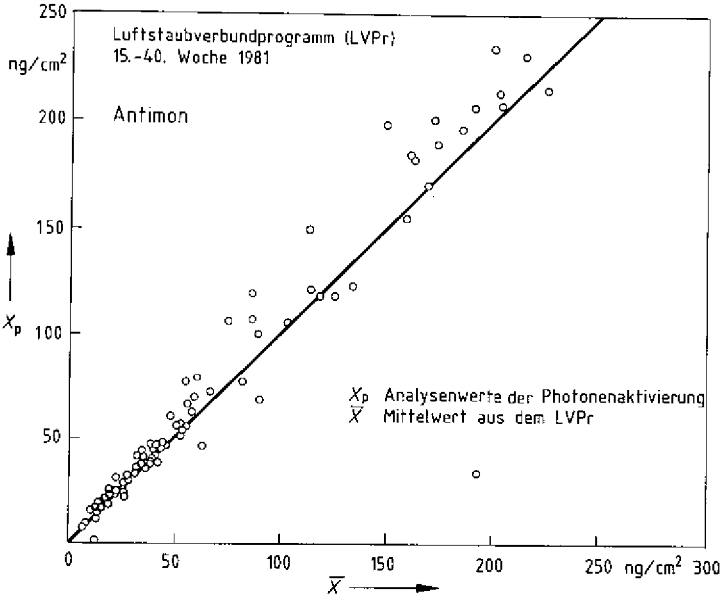

FIGURE 5 Comparison of antimony concentrations (photon activation versus average of all methods used).

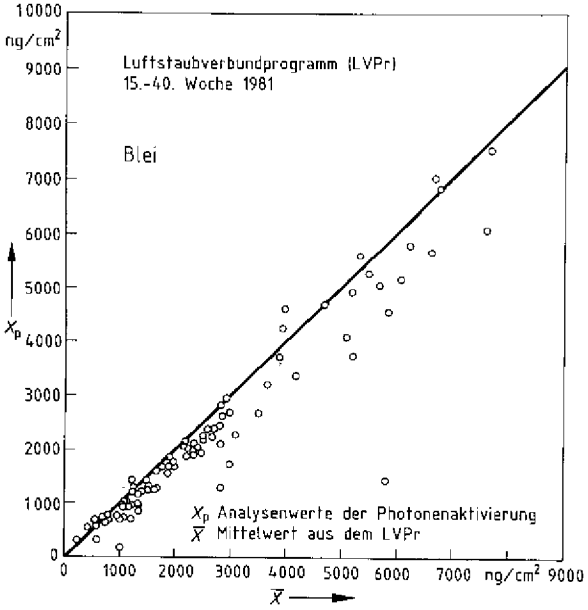

FIGURE 6 Comparison of lead concentrations (photon activation versus average of all methods used).

to slightly deviate systematically; the data tend to be somewhat low. Since a possible source of error is the reference material, this is currently restudied thoroughly for eventual inaccuracy or sources of interference of any kind.

Figure 7 represents the average results of Zn, As, Br and Pb in air dust of five locations sampled over a one year's period.

CONCLUSION

Photon activation analysis has been proved to be a suitable tool for environmental multielement analysis in many cases and so in air particulate analysis. A large part of the elements known as environmental pollutants can be analysed instrumentally with sufficient sensitivity, accuracy and precision.

Some of the particular advantages are the following:

—Other than in many other instrumental methods also light elements (C, N, O, F) can be analysed in ultratrace quantities.

—Elements can be analysed quasi-selectively by proper selection of the irradiation energy and thereby interference through other components can be excluded in many cases if necessary.

—Elements can be analysed whose determination by classical neutron activation analysis—as a competing method—is not possible within the routine multielement analysis procedure (e.g. Ni, Tl).

—Normally there is less influence of the sample matrix to be taken into account than in other instrumental methods.

—Using accelerators with endstanding converters, there are quasi— no restrictions in the sample size; this can be important in strictly non-destructive analysis.

The drawbacks of the method are mainly due to the large instrumental effort; accelerator, sample transfer system and radiation spectrometers are expensive and require continuous maintainance. Moreover, special laboratory installations are necessary to meet the legal radiation protection requirements during activation and activated sample processing.

Finally, the method—as applied to air dust analysis—is unsuitable for the trace analysis of several elements, e.g. sulphur, phosphorus, mercury.

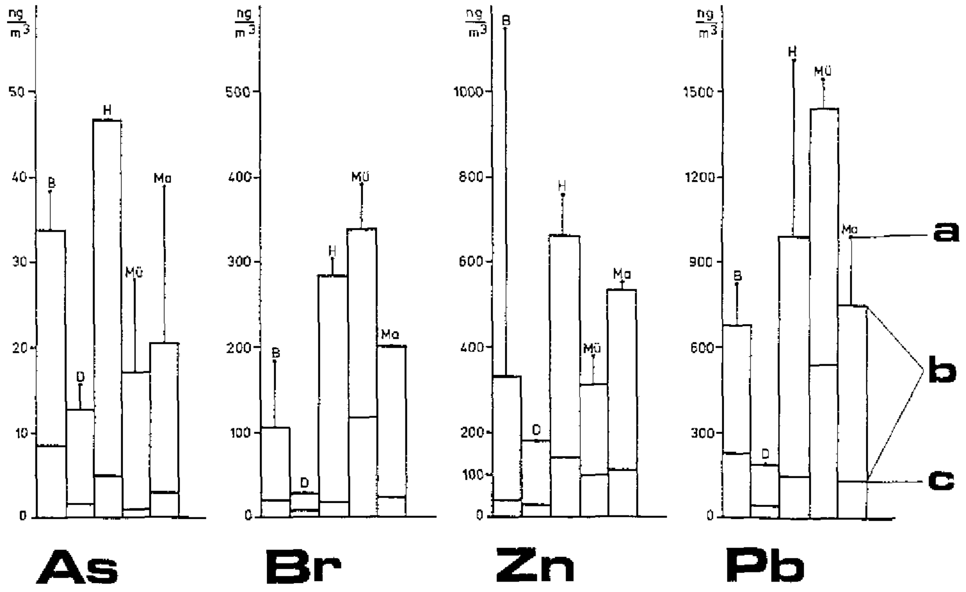

FIGURE 7 Average words for arsenic, bromine, zinc and lead obtained over a one year's collection period. B—Berlin. D—Deuselbach ("clean air" reference). H—Hambrug. Mü—München. Ma—Mannheim. a—uniquely determined maximum concentration. b—normal concentration range. c—minimum concentration.

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