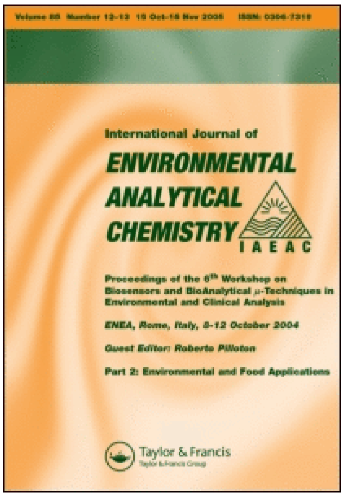

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Neutron Activation Analysis of F, Sc, Se, Ag and Hf in Aerosols Using Short-lived Isotopes

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An 18-sec neutron irradiation of fluorine, scandium selenium and silver produces the following short-lived isotopes: ^{20}F (11.1 s), ^{46m}Sc (18.7 s), ^{77m}Se (17.7 s), ^{110}Ag (24.6 s) and ^{179m}Hf (18.7 s). A 20-sec Ge(Li) count after a 10-sec decay period allows the simultaneous detection of these five isotopes in aerosols. Errors due to fast decay during the counting are minimized by the use of a dead-time stabilizer. The high initial counting rates due to energetic beta rays of short-lived isotopes are reduced by the use of absorbers. Fluorine is also determined, using the threshold reaction ^{19}F(n, p)^{19}O (26.9 s). The interference due to (n, γ) reactions on other impurities in the collected aerosol is reduced by a 30-sec irradiation under cadmium-cover, and a 30-sec count after a 25-sec decay period. The activation of silver and hafnium is enhanced also by an irradiation under cadmium owing to their important resonance peaks. The technique is applied to the analysis of aerosols sampled in Belgium, at urban, industrial and background stations.

INTRODUCTION

Instrumental neutron activation analysis of aerosols, coupled to computer-assisted data reduction has recently been used extensively in air pollution studies.[1–5] It can yield concentration data for 30 to 40 elements, when 2 neutron irradiations and 3 to 5 gamma spectrometric measurements are performed after cooling times ranging from a few minutes to almost a month. In spite of the abundance of information on the inorganic composition of the airborne dust, there are obviously some drawbacks to this technique. The complete information does not become available until one month after sampling and information on important elements such as F and Pb is missing. Although Pb data can easily be obtained by flame or flameless atomic absorption spectrophotometry, F determinations are very difficult. To the best of our knowledge, the only authors giving F concentrations in ambient aerosols deal with spark source mass spectrometry, ion-selective electrodes or colorimetric methods.[6-9] Since quantitative data of the former technique are often subject to large uncertainties, the latter methods give only water-soluble fluorides and require dissolution of the sample, which implies risks of errors due to losses of the volatile fluorine components, and due to contamination. A specific electrode measurement of fluoride further requires a separation of the element from complex-forming metal ions.

NUCLEAR DATA

On neutron irradiation, F produces an 11-sec half-life isotope, ^{20}F, which is a monoenergetic gamma emitter. Henkelmann *et al.*[10] used this reaction for the determination of F in organic compounds and in water. Through NaI gamma spectrometry a detection limit of 1 mcg was obtained in the absence of interfering matrix activities. Unfortunately the thermal neutron cross section is low (Table I). Several other elements have large neutron cross sections for the production of short-lived isotopes. These are Sc, Se, Ag and Hf. All four are generally determined from their long-lived isotopes by a measurement after 20 to 30 days' cooling time. For Ag and Hf the detection limits are, however, often not sufficient. All these elements can be of potential interest because our air pollution studies have shown that the sources and the atmospheric behaviour of these elements are very similar to much larger groups of elements.

TABLE I

Relevant nuclear data of fluorine, scandium, selenium, silver and hafnium[11,12]

Target isotope	Abundance (%)	Cross section (barn)	I_0 (barn)[a]	Product	$T_{1/2}$	Main gamma energies (keV)
^{19}F	100	0.009	0.039	^{20}F	11.1 s	1633.1 (100)
^{45}Sc	100	9	4.9	^{46m}Sc	18.7 s	142.5 (100)
^{76}Se	9.02	20	16	^{77m}Se	17.5 s	161.9 (100)
^{109}Ag	48	88	1112	^{110}Ag	24.6 s	657.8 (100)
^{178}Hf	14	50	980	^{179m}Hf	18.7 s	214.3 (100) 160.6 (10)

[a] Data from Van der Linden *et al.*[16,17]

PROCEDURE

Recently we have constructed a fast pneumatic tube system in the core of the reactor with a transport system of approx. 1 sec and the following neutron spectrum characteristics: $\phi_{\text{therm}} = 4.3 \times 10^{12}$; $\phi_{\text{epi}} = 2.9 \times 10^{11}$; $\phi_{\text{fast}} = 3.1 \times 10^{12}$. Apparently such a spectrum is very convenient for subcadmium epithermal neutron activation. A fraction of the filter, on which approx. 10 mg aerosols is being accumulated, is pressed into a 1.2-cm diameter and 3-mm thickness pellet, and irradiated in this rabbit system. The pellet is irradiated for 18 sec and after a cooling time of 10 sec a 20-sec count is started with a 10% efficiency Ge(Li) detector. A spectrum is shown in Figure 1B, where besides photopeaks of the searched isotopes, also photopeaks can be recognized of the isotopes ^{80}Br ($T_{\frac{1}{2}} = 17.4$ m), ^{28}Al ($T_{\frac{1}{2}} = 2.24$ m), ^{56}Mn ($T_{\frac{1}{2}} = 2.58$ h), ^{116m}In ($T_{\frac{1}{2}} = 54$ m), ^{52}V ($T_{\frac{1}{2}} = 3.75$ m) and

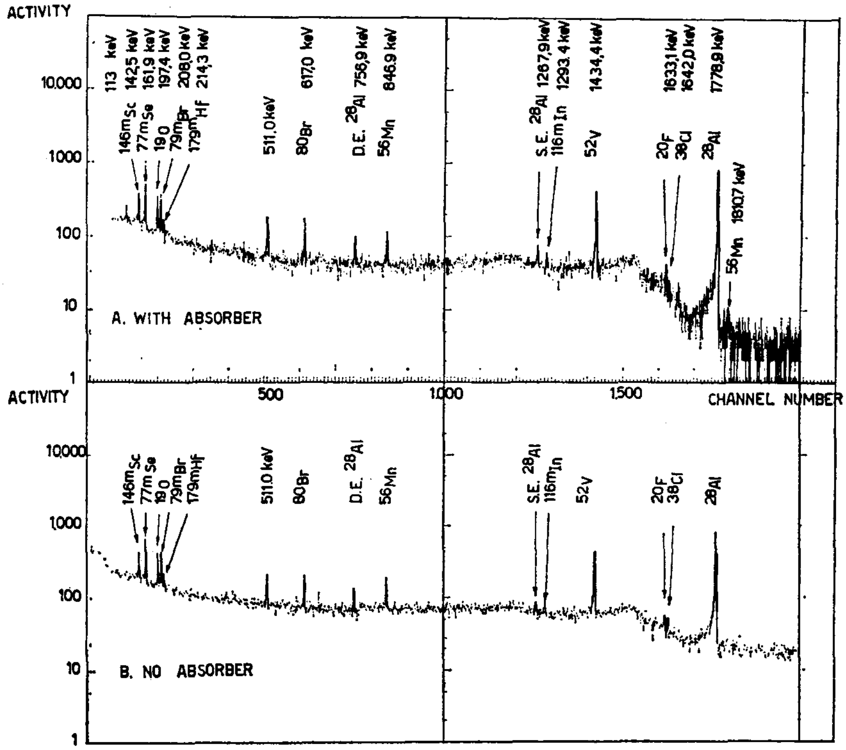

FIGURE 1 Gamma spectrum of aerosol sample, measured with (A) and without (B) a 2.4 g perspex absorber ($T_i = 18$ s; $T_d = 10$ s; $T_c = 20$ s).

^{38}Cl ($T_{\frac{1}{2}}$ = 37.2 m). These elements are routinely detected by a longer measurement after a few minutes' cooling time. The main problem is, however, to obtain reasonably high counting statistics during the short counting time, and still not induce too large a dead-time into the analyzer. Therefore only 2000 channels of a 100 M Hz ADC and a gain setting of 1 keV per channel are used. Furthermore, a perspex absorber of 2.4 g cm^{-2} is inserted in order to reduce the contributions of high energetic beta rays of isotopes such as ^{20}F, ^{24}Na, ^{28}Al, ^{38}Cl, ^{52}V and ^{56}Mn. Figure 1 also illustrates the efficiency of this absorber. Also, errors due to the fast decay of the short-lived isotopes during the counting, which is not corrected for by the regular analyzer dead-time corrections must be minimized or avoided. Therefore a dead-time stabilizer as developed by Bartosek *et al.*[13,14] is used. This stabilizer is based on the automatic creation of additional dead-time at the end of very short live-time measuring intervals, so as to keep the total dead-time constant during the length of the measurement. A 30% dead-time is imposed, since the dead-time initially observed from the counting of the aerosol samples is between 15 and 30%. The standards are made up from a solution of F in strong alkaline medium and a mixed Ag, Se, Sc and Hf solution in nitric acid medium. Both solutions are spotted on a filter paper and also pressed into a pellet. The count rates of the standards are made comparable to the count rate of the unknown samples by an adequate concentration choice. Decay curves showing the variation of the analyzer dead time during the measurement of a sample (curve 1) and a standard (curve 2) are given in Figure 2. In Figure 3 the efficiency of the use of a dead-time stabilizer is investigated. The count rates under the ^{20}F peak are plotted, for a constant amount of F, added to increasing fractions of a same aerosol sample. The amount of aerosol varies from 1 to 12.7 mg whereas the observed dead-time varies from 11 to 23%. When no DTS is used a systematic negative error is obtained at higher dead-times. This is to be expected, as the measuring time is extended by a time equal to the total time the instrument was busy, at a time when the isotope has decayed to approx. 30% of its original activity. When using the DTS, no systematic deviation can be seen, although the number of counts recorded is lower, because the real counting time is reduced from 20 to 14 sec, owing to the imposed 30% dead-time.

Fluorine determination

The determination of F suffers from interference by the ^{23}Na(n, α)^{20}F threshold reaction. For the irradiation conditions used, 1 mg of Na produces an apparent F content of 42±6 mcg (Table II). Na/F ratios in aerosols vary from 10^4 in purely marine aerosols to as low as 1 in polluted industrial or urban air on large continents. Obviously this interference becomes prohibi-

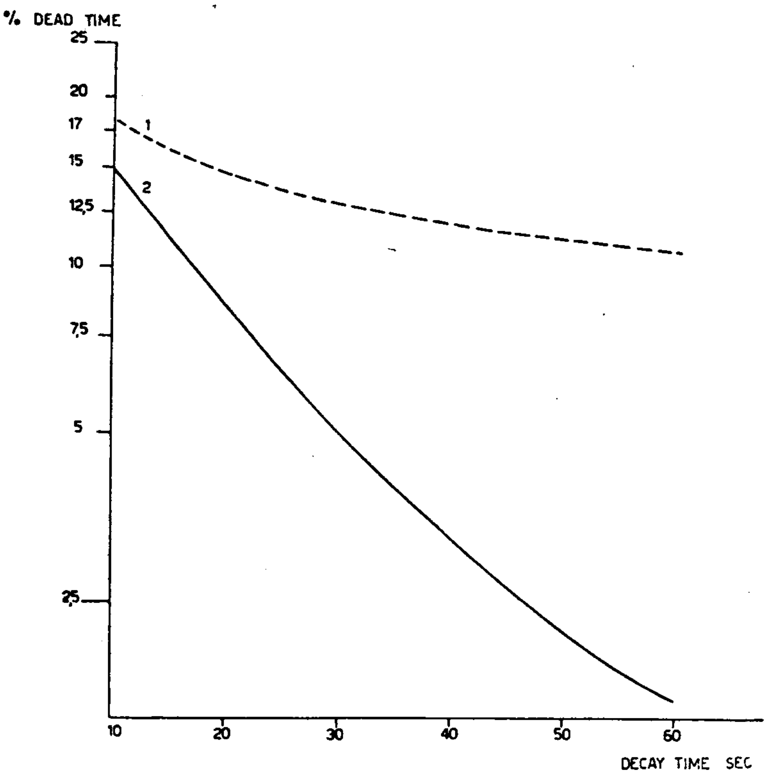

FIGURE 2 Decay of dead-time for aerosol (curve 1) and standard sample (curve 2).

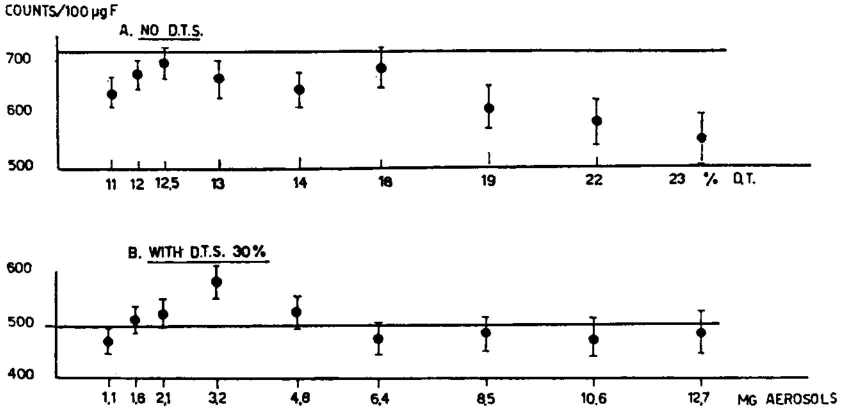

FIGURE 3 ^{20}F activity measured, without (A) and with (B) dead-time stabilizer, as a function of increasing amount of aerosol, or dead-time (T_i = 18 s; T_d = 10 s; T_c = 20 s).

tively large in marine aerosols. In such cases F can also be determined from the threshold reaction $^{19}F(n, p)^{19}O$. ^{19}O has a half-life of 26.9 sec and its most intense gamma radiation has an energy of 197.4 keV. Henkelmann *et al.*[10] used this reaction, with a detection limit of 50 mcg in the absence of oxygen. When using this reaction the prime interference is in fact the (n,γ) reaction on ^{18}O. The cross-section and abundance of ^{18}O are small but in the filter samples oxygen is present in very large quantities. Indeed the cellulose filters used for sampling[15] consist for approx. 50% of oxygen. One fourth or one half of an 11-cm diameter filter contains more than 100 or 200 mg of oxygen. Primarily to reduce this interference an irradiation under 1 mm Cd shielding is performed. The irradiation time is 30 sec, and after a 25-sec cooling a 30-sec count is started. The oxygen content of half a filter induces an apparent content of 77 ± 5 mcg. Since approx. 200 m^3 of air are filtered in a 24-hr period through half a filter, this interference limits the sensitivity to approx. 0.1 mcg F m^{-3}, unless longer samples are taken. The interference due to the oxygen content of aerosols (20–35%) can be neglected. Table III shows a number of F concentrations determined by both activation methods from 24-hr samples. It can be seen that both results generally agree within the standard deviations. Corrections have been made for the Na and O interferences. The sodium contents vary between 0.5 and 3 mcg. m^{-3}. The F concentrations at G.I. are high as compared to those at a residential and background stations in Belgium. Also, 90% of the concentrations determined potentiometrically in the U.S.A. after a dissolution of the samples are lower than 0.05 mcg m^{-3}, which is the detection limit of that method.[7] Existing ambient air quality standards vary between 1 and 10 mcg m^{-3}. This high F concentration at G.I. probably originates from a steel plant or from a superphosphate plant, both in the immediate vicinity of the sampling location.

TABLE II

Relevant data of nuclear reactions of fluorine and interfering isotopes[12]

Target isotope	Abundance (%)	Cross section (mbarn)	Reaction	Neutron flux n. cm^{-2}. s^{-1}	Threshold energy (MeV)
^{19}F	100	9	$^{19}F(n,\gamma)^{20}F$	4.3×10^{12}	—
^{23}Na	100	0.55	$^{23}Na(n,\alpha)^{20}F$	3.1×10^{12}	4.06
^{19}F	100	0.5	$^{19}F(n,p)^{19}O$	3.1×10^{12}	4.22
^{18}O	0.204	0.21	$^{18}O(n,\gamma)^{19}O$	4.3×10^{12}	—

TABLE III

Fluorine concentrations as determined from $^{19}F(n,\gamma)^{20}F$ reaction and from $^{19}F(n,p)^{19}O$ reaction

Sample	TSP (mcg/m^3)	Fluorine conc. (mcg/m^3)			% F in aerosol
		(n,γ) react.	(n,p) react.	Difference	
GI 27/4	62	1.72±0.18	1.84±0.18	−0.12	2.9
GI 27/5	76	0.33±0.13	0.32±0.13	+0.01	0.4
GI 5/6	77	0.40±0.13	0.76±0.19	−0.36	0.7[5]
GI 27/6	146	0.38±0.20	0.58±0.22	−0.20	0.3
GI 2/7	102	0.38±0.14	0.53±0.17	−0.15	0.4[5]
GI 6/7	111	0.38±0.16	0.66±0.20	−0.28	0.5
GI 24/10	85	1.0 ±0.1	1.0 ±0.1	0	1.2
PL 24/10	76	0.10±0.08	< 0.1	—	0.1
DB 24/10	38	< 0.2	< 0.08	—	< 0.2
GR 24/10	69	0.14±0.10	0.17±0.07	−0.03	0.2
LR 24/10	93	0.40±0.10	0.29±0.11	+0.11	0.4

Irradiations under Cd-shielding

Irradiation of aerosols under Cd-shielding is also of interest for other reasons. The activities of the major gamma-producing isotopes such as ^{28}Al, ^{38}Cl, ^{52}V, ^{24}Na and ^{56}Mn are strongly reduced as the ratio of the resonance integral to the thermal neutron cross section is around unity for the production of all these isotopes.[16,17] On the other hand, several barely detectable isotopes have important resonance integrals. In the present investigation the activation of Ag and Hf with a ratio $I_0/\sigma th$ around 15 is enhanced relative to the activation of the most important interfering isotopes. This is illustrated in Figure 4 where spectra are shown from an aerosol sample after irradiations without and with Cd-shielding: since the dead-time is reduced strongly, a much better counting geometry or a larger sample can be used and higher counting statistics can be obtained than those shown in Figure 1. Although more isotopes can be detected after an irradiation under Cd, bromine activities are very important in urban aerosols, as ^{79}Br and ^{81}Br have also high resonance integrals. Figure 5 shows a spectrum of a sample collected in a residential area (AR) in the neighbourhood of a non-ferrous smelter, and after an irradiation under Cd. The photopeaks of ^{77m}Se, ^{116m}In ($T_{\frac{1}{2}}$ = 54 min), ^{80}Br ($T_{\frac{1}{2}}$ = 17.4 min) and even ^{110}Ag are dominant in this spectrum, where also ^{122m}Sb($T_{\frac{1}{2}}$ = 96 s) and ^{124m}Sb ($T_{\frac{1}{2}}$ = 4.2 min) can be recognized. The activation of most of these elements is enhanced by their important resonance peaks. ^{79m}Br ($T_{\frac{1}{2}}$ = 4.9 s) is produced by (n,n') reaction. The lower spectrum in Figure 5 is from an aerosol collected at a marine location (ZB). ^{23}Ne

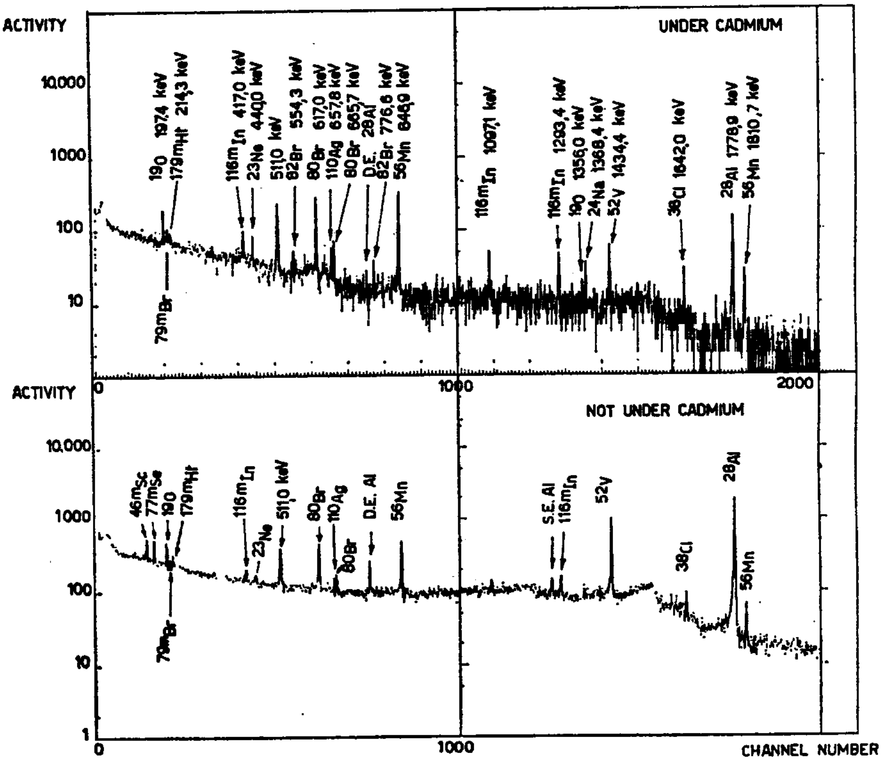

FIGURE 4 Gamma spectrum of aerosol sample after irradiation under cadmium-shielding and after irradiation not under cadmium-shielding ($T_i = 30$ s; $T_d = 25$ s; $T_c = 30$ s).

($T_{\frac{1}{2}}$ 37.6 s) and ^{20}F formed by (n,p) and (n,α) reaction on ^{23}Na are major peaks in this spectrum.

APPLICATION

In October 1972, a 14-station sampling network over Belgium was started.[18] Samples for all 14 stations, from several days have already been analysed for 45 components by several techniques of analysis including the present procedure.[19] Tables IV and V give some results for Sc and Se from urban (AR, CR), industrial (GI, LI) and continental and marine background stations (DB, ZB). The results are compared to those obtained by activation analysis using the long-lived isotopes ^{46}Sc ($T_{\frac{1}{2}} = 83.8$ d) and ^{75}Se ($T_{\frac{1}{2}} =$ 120 d). In Table VI some Hf results are given, as obtained by thermal neutron

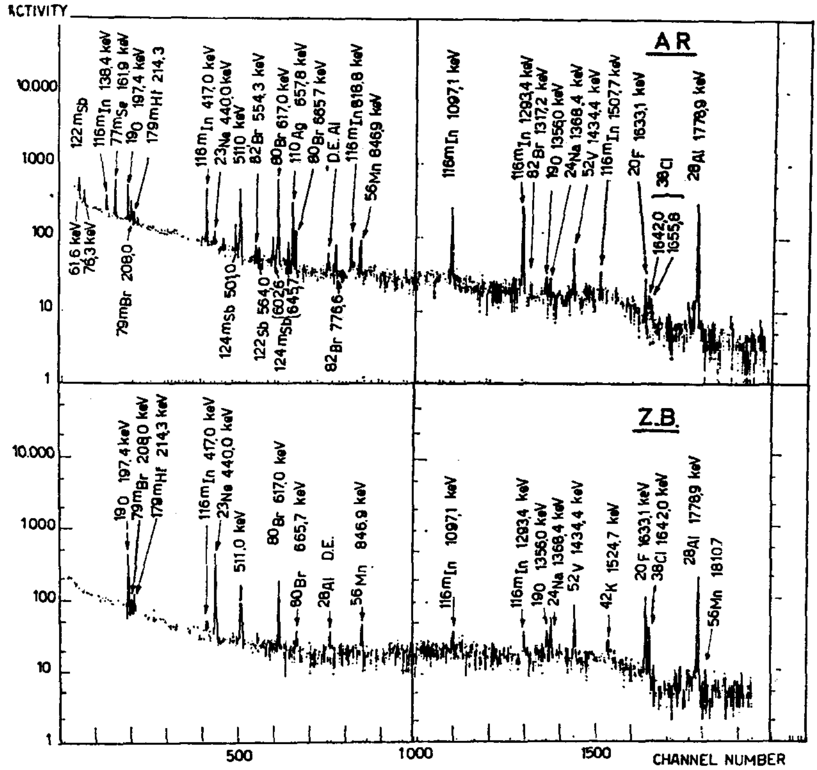

FIGURE 5 Gamma spectrum of aerosol sampled in residential area (AR) and at a marine location (ZB) after irradiation under cadmium-shielding ($T_i = 30$ s; $T_a = 25$s; $T_c = 30$ s).

activation and by activation under Cd-shielding, both using the short-lived isotope ^{179m}Hf. As expected, the results after irradiation under Cd are more precise.

Figure 6 shows the variations of the concentrations on six daily samples taken in Gent during a period of unusually high pollution levels, in September 1972, for the total suspended particulate (TSP), F, Sc, Se, Ag and Hf. For sample V standard deviations of the analytical results are shown. It can be seen that concentration variations occur with a factor of 10 for TSP, Hf and F. Similar variations are found for anthropogenically produced pollution components, such as SO_4^{2-}, NO_3^-, NH_4^+, organics extractable in benzene, V, I, etc.[20] The peak concentrations on the fourth day are mainly due to the extreme stability of the air, with nearly no wind at all during the entire sampling period. The variation of the Sc concentrations is rather similar but with a relatively high concentration for all three samples III, IV, and V. This

TABLE IV

Scandium concentrations as determined from short-lived (^{46m}Sc) and from long-lived (^{46}Sc) isotope

Sample	TSP (mcg/m^3)	Sc conc. (ng/m^3)			ppm Sc in aerosol
		^{46m}Sc	^{46}Sc^{20}	Difference	
AR	142	0.60±0.16	0.51±0.10	+0.09	3.9
CR	70	0.66±0.06	0.73±0.06	−0.07	10
GI	85	0.35±0.06	0.32±0.05	+0.03	4.0
LI	119	0.52±0.07	0.56±0.06	−0.04	4.0
DB	38	0.25±0.04	0.23±0.04	+0.02	6.3
ZB	101	0.11±0.04	0.15±0.03	−0.04	1.3

TABLE V

Selenium concentrations as determined from short-lived (^{77m}Se) and from long-lived (^{75}Se) isotope

Sample	TSP (mcg/m^3)	Se conc. (ng/m^3)			ppm Se in aerosol
		^{77m}Se	^{75}Se^{20}	Difference	
AR	142	119±2	117±2	+2	830
CR	70	2.5±0.5	3.0±0.5	−0.5	33
GI	85	8.1±0.5	8.5±0.5	−0.4	98
LI	119	2.2±0.5	2.5±0.5	−0.3	20
DB	38	2.1±0.3	2.0±0.3	+0.1	54
ZB	101	2.3±0.4	2.0±0.3	+0.3	21

TABLE VI

Hafnium concentrations as determined by irradiation under cadmium and not under cadmium

Sample	TSP (mcg/m^3)	Hf conc. (ng/m^3)			ppm Hf in aerosol
		Thermal	Epithermal	Difference	
AR	142	0.09+0.08	0.14±0.06	−0.05	0.85
CR	70	0.29±0.04	0.28±0.03	+0.01	4.0
GI	85	0.07±0.04	0.11±0.02	−0.04	1
LI	119	0.42±0.05	0.38±0.03	+0.04	3.4
DB	38	0.09±0.03	0.06±0.01	+0.03	2
ZB	101	0.05±0.03	0.04±0.01	+0.01	0.4

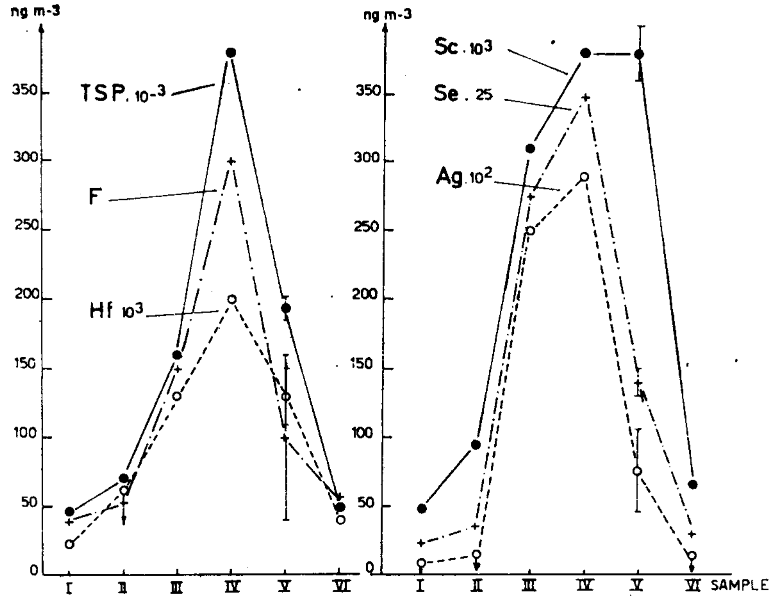

FIGURE 6 Concentration variations of TSP, F, Hf, Sc, Ag and Se during 6 days, from a period of unusually high pollution.

behaviour is typical for a large group of non-volatile elements such as Si, Al, Fe, Co. La, Ce, Sm, Ba and Th, all elements which may be soil-derived and have many sources in populated areas. The Se pattern is different because of its relatively high concentration for sample III. This element has a typical behaviour of other relatively volatile non-ferrous metals such as As and Sb. Silver is remarkable because of its larger variation, with more than a factor 30. The extreme samples are so low, that only higher limits can be obtained by the analysis. The amounts of Ag collected are indeed lower than the blank value of the paper for samples I, II and VI. This Ag pattern is found to be typical for elements such as Cu, Cd, In, Hg and Au. The high concentrations of the Ag and Se groups for sample III can be explained by the eastern wind during that sampling day. Towards the East of the sampling site, there is indeed an important non-ferrous industry. Similar groupings of elements were obtained from other air pollution studies in Belgium, such as from our 14-station network and by measurements of mass versus particle size distributions. As a matter of fact these groups are not universal constants and can be subject to changes in the vicinity of important sources. In Gent, for example, the elements Mn, Ti, Ca, K and PO_4^{3-} form a separate group owing to the presence of important sources of these components to the north of Gent.[21] Na and Cl are mainly marine-derived elements and Br with Pb originate in urban areas primarily from automotive emissions. Although a longer count after a few minutes' cooling is more appropriate for elements such as Mn, Na, Cl and Br, they can also be determined from the same short counting procedure.

CONCLUSION

The present procedure allows a very fast nondestructive determination in aerosols of five elements which are all of potential interest. Air pollution studies in Belgium have indeed indicated, that Sc, Se, Ag and Hf can be considered as indicators for the main groups of elements or components, present in the aerosol, namely the soil derived elements, the volatile pollution elements, a number of non-ferrous metals, and the large group of anthropogenically produced pollution components with distributed sources. If required, a number of other elements, such as Al, V, Cl, Na, Br, Mn, In, etc., with indicators of other groups, such as marine or automotive aerosols, can also be determined by the same procedure. Furthermore, the element F, which is difficult to be analysed accurately by other techniques, can be determined by two alternative activations. It is therefore stated that a very short activation-counting procedure can give in a few minutes an overview of the composition of the particulate pollution.

The investigation has also illustrated that by the use of absorbers and a DTS, initial high count rates are acceptable for the measurement of short-lived isotopes. Finally, this work has indicated the potential interest of irradiations under Cd-shielding, in the instrumental neutron activation analysis of aerosols.

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