ISTITUTO NAZIONALE DI FISICA NUCLEARE

Sezione di Milano

INFN/TC-99/16
10 Agosto 1999

TRACE ELEMENT MONITORING IN TOTAL AIR PARTICULATE AND IN INHALABLE FRACTIONS INVESTIGATED BY NEUTRON ACTIVATION ANALYSIS

D. Arginelli[1], C. Birattari[1], M. Bonardi[1], M. Gallorini[2], L. Gini[1], F. Groppi[1] and E. Rizzio[2]

[1] L.A.S.A. – INFN–Sezione di Milano, Dip. Fisica Università di Milano,
via F.lli Cervi 201, I–20090 Segrate (Mi), Italy
[2] CRAA, CNR and INFN–Sezione di Pavia, via Taramelli 12, I–27100 Pavia, Italy

Abstract

The concentration of 27 trace elements have been determined in the total air particulate matter as well as in its inhalable size segregated fractions collected in urban, industrialised and rural–residential areas in the North of Italy. By means of multistage inertial impactors trace element granulometric distribution has been measured in the PM10 (particles with an Equivalent Aerodynamic Diameter –AED– of less than 10 μm) and in its subsequent "respirable" fractions (alveolar, bronchial and tracheo–pharynx), which contain particles with nominal diameter from 0 to less than 9 μm.
All of the measurements have been carried out by Instrumental Neutron Activation Analysis (INAA).
For all investigated elements the granulometric distribution trends found in different locations are reported and compared.

PACS.: 92.60.S

*Published by **SIS–Pubblicazioni***
Laboratori Nazionali di Frascati

1 INTRODUCTION

The monitoring of trace element (TE) content in the atmospheric particulate may contribute to control and evaluate the degree of the air pollution and furnishes additional information for assessing the air quality of our environment 1). Many TE of anthropogenic origin may be considered dangerous to the human health and their presence in the air constitute a potential risk for the population, not only at level of threshold concentrations, but also in terms of prolonged exposure to low levels 2). However, the knowledge of the concentrations in the total suspended air particulate, which represents an important parameter, is nevertheless not sufficient for a more close evaluation of the possible impact onto the public health. The monitoring must be comprehensive of the concentrations in the fine particulate fractions involved in the respiratory system at alveolar and bronchial levels. By means of inertial multistage impactors, the air particulate has been collected in fractions, to distinguish among the deposition in the alveolar (particles from 0 to 1.1 μm nominal diameter), bronchial (from 1.1 to 4.6 μm) and tracheo-pharynx (from 4.6 to < 9 μm) areas of our respiratory system. In the frame of this work two sampling campaigns (dust collection upon filters, by aspiration) were carried out during winter 3) (February-March) and summer (June-September) 1998, in an urban area (Milan downtown), in a suburban-industrialised area (Segrate) and in a rural-residential area (Ispra) 4). Instrumental Neutron Activation Analysis 5,6,7) (INAA) and Electrothermal Atomic Absorption Spectrophotometry (ETAAS) were employed to evaluate the concentration in ng/m^3 of many elements, of toxicological interest. From the overall data got in this study two main observations can be made. The concentration of the TE in the corresponding total air particulate allows us to compare the state of the air quality among the different locations investigated. The knowledge of the TE distribution trends in the different size particle fractions furnishes information about their mobility and their paths followed in the different human respiratory areas. The main analytical problem, for the TE determination, arises from the very low concentrations 8) to be determined and the contribution from the blanks of the filtering membranes 9,10), employed in sampling procedures. Samplings of 48 hours each were carried out to increase the amount of air particulate matter collected in the rural-residential area in order to obtain a better mass loaded/filters-blank ratio. All the analytical data were corrected for the blank contribution, by carrying out replicate analyses of the trace element content in the filtering membranes.

2 MATERIAL AND METHODS

2.1 Sampling

Two sampling campaigns were carried out during winter (February-March) and summer (June-September) 1998, in an urban area (Milan downtown), in a suburban-industrialised area (Segrate) and in a rural-residential area (Ispra). Two series of independent samplings were carried out in each location, obtaining two sets of samples for the analysis by INAA and ETAAS, performed by the nuclear reactor of the University of Pavia and by CNR of Pavia respectively. The second technique allowed to study some elements (Pb, Cd, Ni and Cu) that it would be impossible to investigate by INAA.

In order to reproduce human condition of breathing, samples were collected onto cellulose filters, at 170 cm height from ground, with a flux rate of 18 l/min, for the total air particulate and of 28 l/min for the collection of the fractions of different size.

The sampling times, depending on the supposed pollution level, were of 24 h in Milan and Segrate and of 48 h in Ispra.

In the case of total air particulate the samples were collected onto 0.8 μm cellulose filters (Sartorius – Germany) of 4.5 cm diameter.

As far as granulometric distribution is concerned two systems, of inertial particle sizing samplers (Graseby Andersen Ltd - USA), were used to collect the granulometric fractions of the air particulate. The first is composed of 8 stages and uses 9 cm diameter and 0,8 μm porosity Millipore filters, the second is composed of 9 stages and uses 8 cm diameter and 0,8 μm porosity Millipore filters as well. At 1 ACFM[1] both 8 and 9 stage systems have similar ECD (Effective Cutoff Diameter) corresponding to the following nominal ranges in μm: 1 (0-0.41), 2 (0.41-0.70), 3 (0.70-1.1), 4(1.1-2.2), 5 (2.2-3.3), 6 (3.3-4.6), 7 (4.6-6.0), 8(6.0-9.0 or10), preseparator >9 (or >10) 11).

During the whole sampling periods the weather conditions were constant and characterised by thermal inversion (cool sunny days, high pressure, no wind). In these weather conditions maximum air pollution levels are reached.

2.2 Standard and blanks

The evaluation of concentration of sampled elements was carried out with a comparison technique, irradiating both samples and standard multielement solutions in the same condition of geometry and neutron flux.

So for the analyses by INAA, series of multielement standard solutions and of SRM[2], produced and certified by the N.I.S.T.[3], were prepared and used in dependence of the nuclear characteristics and the sensitivity of the elements to be determined.

A special effort was devoted to evaluate the blanks of the filters used in the samplings. To this purpose, series of filters were analysed in the same way of the samples to check the trace elements impurity. Table 1 reports the results obtained in all the blanks

---

[1] 1 ACFM: one Air Cubic Feet per minute, which correspond to a flux rate of 28 l/m.

[2] Standard Reference Material

[3] National Institute of Standards & Technology

analysis. The data are the mean of the values obtained in the analysis of 4 filters, for each type, coming from different batches.

TAB 1: Blank values in ng per filter of the trace elements determined in the filtering membranes used to collect the air particulate.
Data obtained from the analysis of 4 filters of each type.

Element	**Sartorius** 0.8µm 47mm Ø ng/filter	**Millipore** 0.8µm 80mm Ø ng/filter	**Millipore** 0.8µm 90mm Ø ng/filter
As	1,9 ± 0,9	1,4 ± 0,8	1,3 ± 0,8
Au	3,6E-02 ± 4,4E-03	0,2 ± 0,04	0,1 ± 2,8E-02
Br	49,1 ± 7,2	51,4 ± 15,8	52,3 ± 22,1
Ce	3,3 ± 3,2	1,4 ± 0,8	4,6 ± 5,9
Cl	10613,2 ± 1662,2	39500 ± 7900	46516,0 ± 16513,5
Co	3,0 ± 1,4	1,6 ± 0,4	7,2 ± 5,4
Cr	15,6 ± 10,3	142,2 ± 79	387,3 ± 175,1
Fe	900,3 ± 185,4	790 ± 316	1480,1 ± 806,6
Hf	3,0E-01 ± 4,8E-01	<0,4	0,53 ± 0,51
Hg	0,5 ± 4,5E-01	<0,4	1,5 ± 1,4
I	5,1 ± 2,5	9,5 ± 3,2	18,8 ± 7,4
K	380,0 ± 180,0	1975 ± 237	2300,0 ± 500,0
La	1,1 ± 0,6	1,2 ± 0,4	1,4 ± 0,2
Mg	52602,3 ± 28681,8	1343 ± 316	8507,5 ± 2408,9
Mn	28,9 ± 6,5	27,7 ± 7,9	45,5 ± 35,8
Mo	4,2 ± 3,6	0,7 ± 0,2	1,5 ± 0,8
Sb	4,0 ± 2,3	3,8 ± 0,9	3,34 ± 0,97
Sc	0,1 ± 0,07	<0,04	0,11 ± 0,05
Sm	0,6 ± 0,3	0,03 ± 0,001	0,7 ± 0,2
Ti	546,3 ± 126,2	232,3 ± 94,8	351,1 ± 87,8
V	0,6 ± 0,2	1,24 ± 0,4	6,5 ± 6,4
Zn	271,7 ± 83,4	948 ± 316	2359,1 ± 789,1

The differences between the Sartorius and the Millipore, being both of cellulose, are mainly due to the different size of the filters. For both type of filters the quite large spread in the standard deviation is probably due to the disomogeneity among the filters. For some elements, significative variations between the same type of filters, coming from different batches, have been also found, this reflects the fact that impurities may not be homogeneously distributed. To correct the final analytical results the average values of blank data have been used. The correction was mandatory for almost all the elements considered and in particular for Br, Cl, Cr, Fe, Mn, Mg, Ti e Zn. In the case of the samples collected in the low polluted area of Ispra the blank contribution is often greater than the element concentration. In this area the minimum sampling time to obtain an acceptable ratio between the amount of air dust and the filters blank was 48 h. The blank arising from the plastic containers, in which the samples were sealed for the neutron irradiation, were evaluated only for the elements determined by short irradiation (V, Mg, Ba, Mn, Cl, Ti, I) since, for all the others, the samples were transferred, after irradiation, in clean, non irradiated plastic counting vials.

3 ANALYSES

INAA is a powerful nuclear technique that allows to study a great number of elements by the bombardment of stable isotopes and the successive gamma spectrometry of the activated samples. The TRIGA Mark II (General Atomic – USA) research nuclear reactor of the University of Pavia was employed for the neutron irradiations. According to the type of the analysis two different irradiation procedures have been used. The pneumatic irradiation facility “Rabbit” (sample transfer time 3.5s) was used for short irradiations (300 s), at a neutron flux of $5X10^{12}$ cm^{-2} s^{-1}, to study short half life produced radioisotopes. Long-term irradiations (20-25 h) were performed in the reactor central thimble facility “Lazy Susan”, at a neutron flux of 10^{13} cm^{-2} s^{-1}, to study medium and long half life produced radioisotopes. For the gamma spectra evaluation HPGe detectors, coupled to multichannel analysers (ORTEC and Quantum MCA, ANS) were used. For medium and long counting, automatic sample changers were coupled to the systems.

The use of reference standards allows the quantitative evaluation of each element, present in a sample, without any problem of efficiency, if all irradiation and measurements are made in the same location, geometry and time.

Under the same conditions of bombardment and measure the specific activity is the same, both in the standard and in the filter. So it is possible to determine the mass of an element, present in a sample, by the ratio of its activity to the specific activity induced in the standard for the same element. Moreover all samples (filters and standards) have been measured for the same interval of live time and the same gamma emission has been taken into consideration. For this reason the following formula (1) can be used to determine the mass m_C of each element in a sample.

$$m_C = m_{el} \frac{C_C \cdot e^{\lambda \cdot t_{EOB\ C}} \cdot \dfrac{t_{real\ C}}{1 - e^{-\lambda \cdot t_{real\ C}}}}{C_S \cdot e^{\lambda \cdot t_{EOB\ S}} \cdot \dfrac{t_{real\ S}}{1 - e^{-\lambda \cdot t_{real\ S}}}} \tag{1}$$

where m_{el} is the mass of the element in the standard, obtained by the product of the concentration of that element, in μg/g, certified in the standard, and the mass of the standard measured by weighting; C_C is the photopeak net count of the element in the sample; C_S is the photopeak net count of the element in the standard, without the contribution of the blank, calculated as the mean value of three plastic vials; t_{EOB} is the waiting time, or the time that passes from the end of bombardment and the beginning of the measure; t_{real} is the real time of measure; the two exponential terms are correction factors for the decay during the waiting time and for the decay during acquisition, of both the sample (numerator) and the standard (denominator).

Now the concentration of an element, in ng/m^3 is calculate as the ratio between the mass, obtained by (1), and the collected air volume.

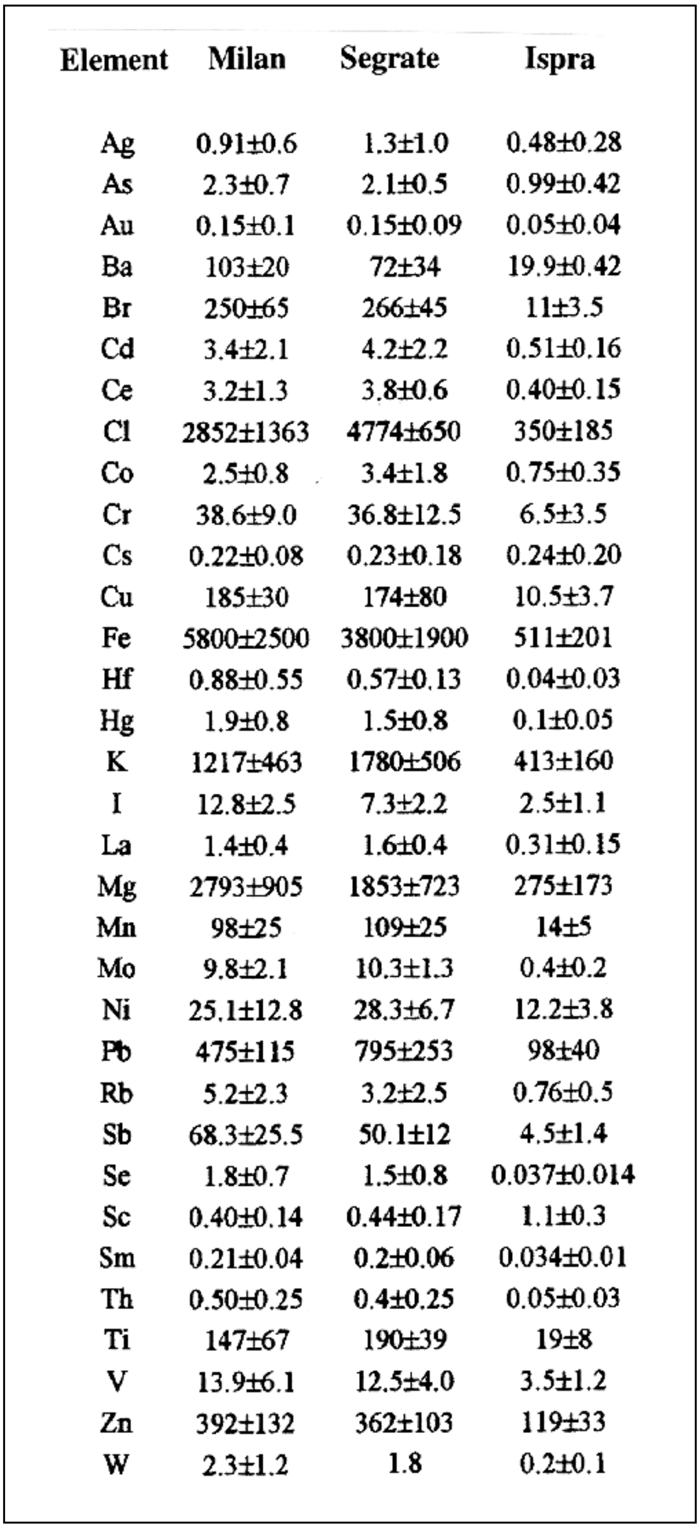
4 RESULTS AND DISCUSSION

4.1 Total concentrations

The average concentrations (ng/m^3) of the analysed elements of the particulate matter collected, during the winter and summer campaigns respectively, in the specified three locations, are listed in Table 2 and Table 3. The standard errors reported in Table 2 are calculated as the mean standard deviation of four samples for each location, while those reported in Table 3 are obtained using only two samples for the first two locations. In the case of Ispra only one measure was available so no standard deviation is reported.

The majority of the elements determined in the winter campaign samplings shows concentration values with a quite reduced standard deviation (usually very large in this type of analyses) reflecting the fact that the weather conditions, during the collection period, were constant and did not introduce significative changes in the composition of the air particulate.[12)] Unless for lead and few other elements no appreciable differences between the concentrations in Milan area and Segrate area can be noted. The higher Pb value in Segrate area may be attributed to the presence of the nearby Milan east-beltway which may be considered one of the highway with the heaviest automotive traffic in Italy. In any case the data demonstrate that the pollution rate between the two areas (metropolitan and suburban-industrialised) is similar and the TE concentrations are of the same order of magnitude. On the contrary, the comparison with the Ispra values shows, for all the elements, a totally different situation. Here, all the elements and in particular those which can be assumed released from anthropogenic sources are present with much lower concentrations. Differences in concentration ranging between 5 and 48 times are registered for elements such as V, Pb, Cr, Cd, Fe, Hg, W, Sb, Cu, Mo and Se. Unless Sc, the same trend, but with lower variations, can be noted for elements that may be considered of natural origin (crustal and soils composition) such as K, La, Mg, Ba, Ti.

TAB. 2: Concentration values in ng/m^3 of some elements in the total air particulate of Milan downtown, Segrate and Ispra determined in February 1998



Element	Milan	Segrate	Ispra
Ag	0.91±0.6	1.3±1.0	0.48±0.28
As	2.3±0.7	2.1±0.5	0.99±0.42
Au	0.15±0.1	0.15±0.09	0.05±0.04
Ba	103±20	72±34	19.9±0.42
Br	250±65	266±45	11±3.5
Cd	3.4±2.1	4.2±2.2	0.51±0.16
Ce	3.2±1.3	3.8±0.6	0.40±0.15
Cl	2852±1363	4774±650	350±185
Co	2.5±0.8	3.4±1.8	0.75±0.35
Cr	38.6±9.0	36.8±12.5	6.5±3.5
Cs	0.22±0.08	0.23±0.18	0.24±0.20
Cu	185±30	174±80	10.5±3.7
Fe	5800±2500	3800±1900	511±201
Hf	0.88±0.55	0.57±0.13	0.04±0.03
Hg	1.9±0.8	1.5±0.8	0.1±0.05
K	1217±463	1780±506	413±160
I	12.8±2.5	7.3±2.2	2.5±1.1
La	1.4±0.4	1.6±0.4	0.31±0.15
Mg	2793±905	1853±723	275±173
Mn	98±25	109±25	14±5
Mo	9.8±2.1	10.3±1.3	0.4±0.2
Ni	25.1±12.8	28.3±6.7	12.2±3.8
Pb	475±115	795±253	98±40
Rb	5.2±2.3	3.2±2.5	0.76±0.5
Sb	68.3±25.5	50.1±12	4.5±1.4
Se	1.8±0.7	1.5±0.8	0.037±0.014
Sc	0.40±0.14	0.44±0.17	1.1±0.3
Sm	0.21±0.04	0.2±0.06	0.034±0.01
Th	0.50±0.25	0.4±0.25	0.05±0.03
Ti	147±67	190±39	19±8
V	13.9±6.1	12.5±4.0	3.5±1.2
Zn	392±132	362±103	119±33
W	2.3±1.2	1.8	0.2±0.1

TAB 3: Concentration values (ng/m^3) in the total air particulate determined in Summer 1998

element	**Milan**	**Segrate**	**Ispra**
As	1,8 ± 0,6	2,3 ± 2,1	2,5
Au	2,8E-02 ± 1,7E-03	3,1E-02 ± 1,6E-02	1,3E-01
Br	19,4 ± 2,5	15,5 ± 2,3	6,1
Ce	1,2 ± 0,6	1,3	3,5E-01
Cl	534,7 ± 377,2	234,7 ± 134,1	136,2
Co	1,1 ± 0,6	0,6 ± 0,7	0,3
Cr	10,1 ± 1,7	11,3 ± 7,6	3,3
Fe	1802,0 ± 268,6	683,4 ± 957,7	294
Hf	0,4 ± 0,2	0,1 ± 0,1	2,3E-02
Hg	0,1 ± 0,1	0,15 ± 0,04	1,4E-02
I	2,3 ± 0,4	2,3 ± 0,7	1,5
K	340,8 ± 481,9	335,7 ± 347,7	299,0
La	0,5 ± 0,2	0,4 ± 0,4	0,1
Mg	633,1 ± 204,0	663,7 ± 170,9	834,5
Mn	29,2 ± 0,4	25,9 ± 0,7	10,5
Mo	8,0 ± 3,4	1,4 ± 1,2	3,4
Rb	0,4 ± 0,04	4,0	0,2
Sb	10,2 ± 3,8	3,5 ± 2,6	1,3
Sc	0,2 ± 0,026	0,1 ± 0,2	2,8E-02
Se	0,4 ± 0,15	1,3 ± 1,3	8,7E-01
Sm	0,2 ± 0,1	0,3 ± 2,5E-01	2,4E-01
Th	0,2 ± 0,024	0,2	4,3E-02
Ti	64,7 ± 15,7	66,6 ± 15,7	8,1
V	3,6 ± 1,9	3,2 ± 1,5	1,6
Zn	173,8 ± 43,5	119,0 ± 57,1	109,6

Among the elements determined in the summer campaign, as reported in Table 3, we can notice that for some elements such as Br and V it seems to be a substantial difference between the concentrations found in Milan and Segrate and those found in Ispra. Br and V derive from combustion processes, such as automotive traffic and heating. During summer time there is only the first cause of pollution, which in the rural area is less present than in the other two areas. Also for other elements such as Ti and Sm the concentration in Milan and Segrate is greater than that found in Ispra. This is due to the fact that these two elements as well as La and Mg, of crustal origin, are bound to movimentation and suspension of powder from the ground.

In conclusion, as far as the TE concentration in the total suspended air particulate is concerned, the results reported here can be representative of the actual air quality standards of the investigated areas and can be used to characterise the composition of the corresponding aerosols.

4.2 Granulometric distribution

As previously mentioned, the distribution of the TE in the different inhalable and respirable size-fractionated particles gives information on their specific pathway followed in the human respiratory system. This has particular importance for those elements of anthropogenic origin which, deriving from chemical combustion processes, are contained in the fine particulate fractions. By the multistage impactors used in this work the concentrations in the 8 (or 9) single stages have been measured. Nevertheless, in order to make a best correlation between size particle fractionation and the different respiratory tracts, the data have been grouped in six granulometric intervals as follows: alveolar (0-0.4 µm) - (0.4-0.7 µm) - (0.7-1.1 µm); bronchial (1.1-2.1 µm) - (2.1-4.6 µm); tracheo-pharynx (4.6-9 µm).

Examples of typical granulometric distribution trends are given in Figures 1 and 2 in which the diagrams of the concentrations in ng/m^3 versus the particle fractions in µm (ECD) for the three locations object of study, for some of the elements analysed are reported. In all figures a vertical bar separates the three values associated with the alveolar fraction from the other components, to better underline the trend of the finest particles. Figure 1 shows the behaviour of As, Br and V which can be considered associated to anthropogenic emissions (chemical process, industrial activities, combustion), to automotive emissions (Br and V) and, as in the case of V, also to the fossil fuel (oil) heating. All these elements show a similar trend with higher concentrations associated to the finest particles which are typically present in the emissions of combustion processes. However, the relative concentrations differ sensibly between the urban-industrialised (Milan and Segrate) and the rural-residential (Ispra) areas, being, the values found in these last, much lower. The presence of As in the rural area is comparable to that of the more contaminated areas, and this may be due to long distance transport phenomena which can introduce into the “clean” areas the most mobile fraction released from the far pollutant emission points. A totally different behaviour can be observed for those elements not originated from pollution sources and related to the natural crust and soils composition. As example, Figure 2 shows the granulometric distribution of Mg, Sc and La. The trends are similar for all the elements in the three locations with the higher concentrations associated to the largest particles.

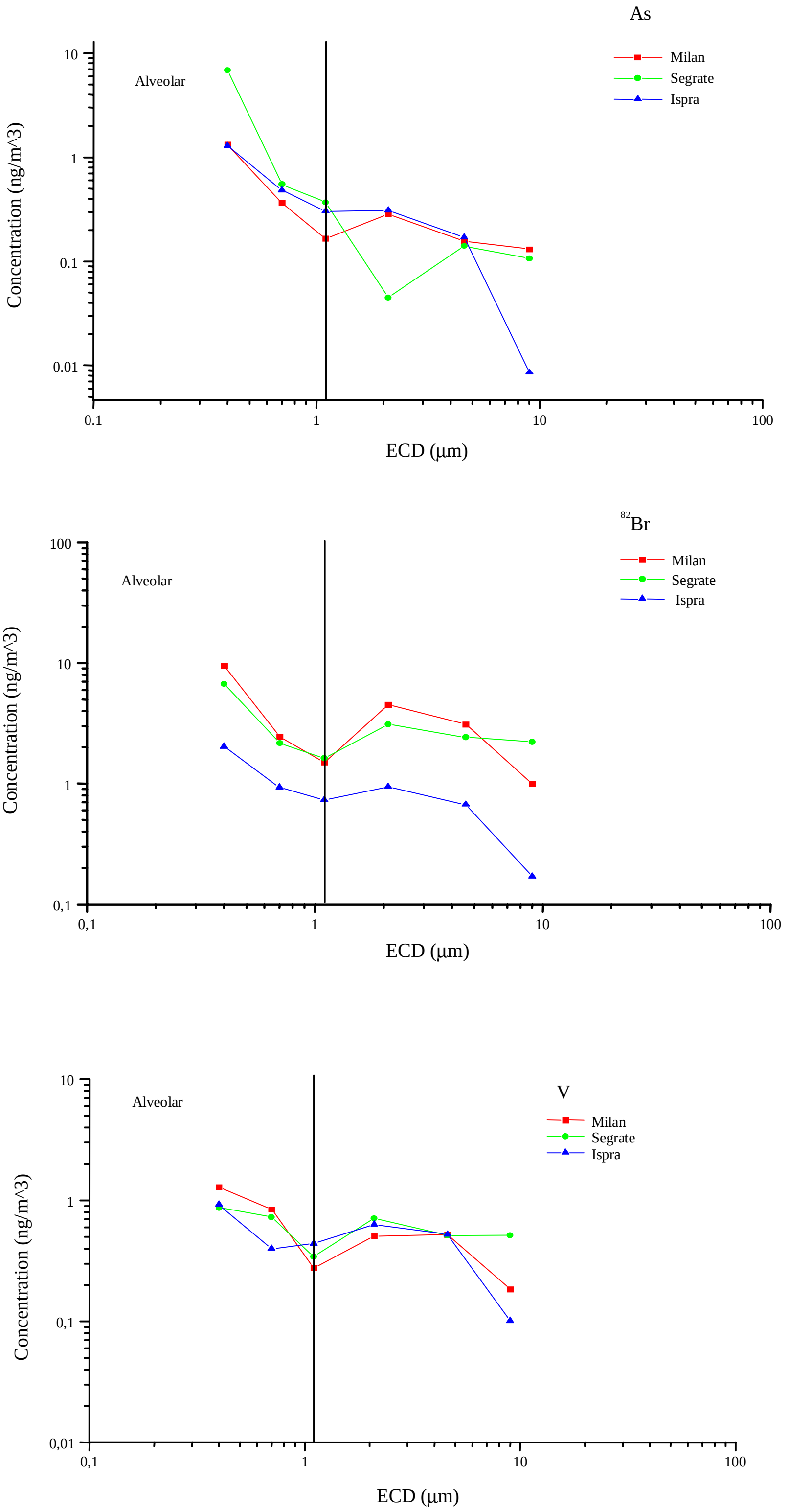


FIG. 1: Particle size distribution of some anthropogenic elements (As, Br and V) in the airborne particulate matter of urban, suburban-industrialised and rural residential areas of north Italy (summer 1998).

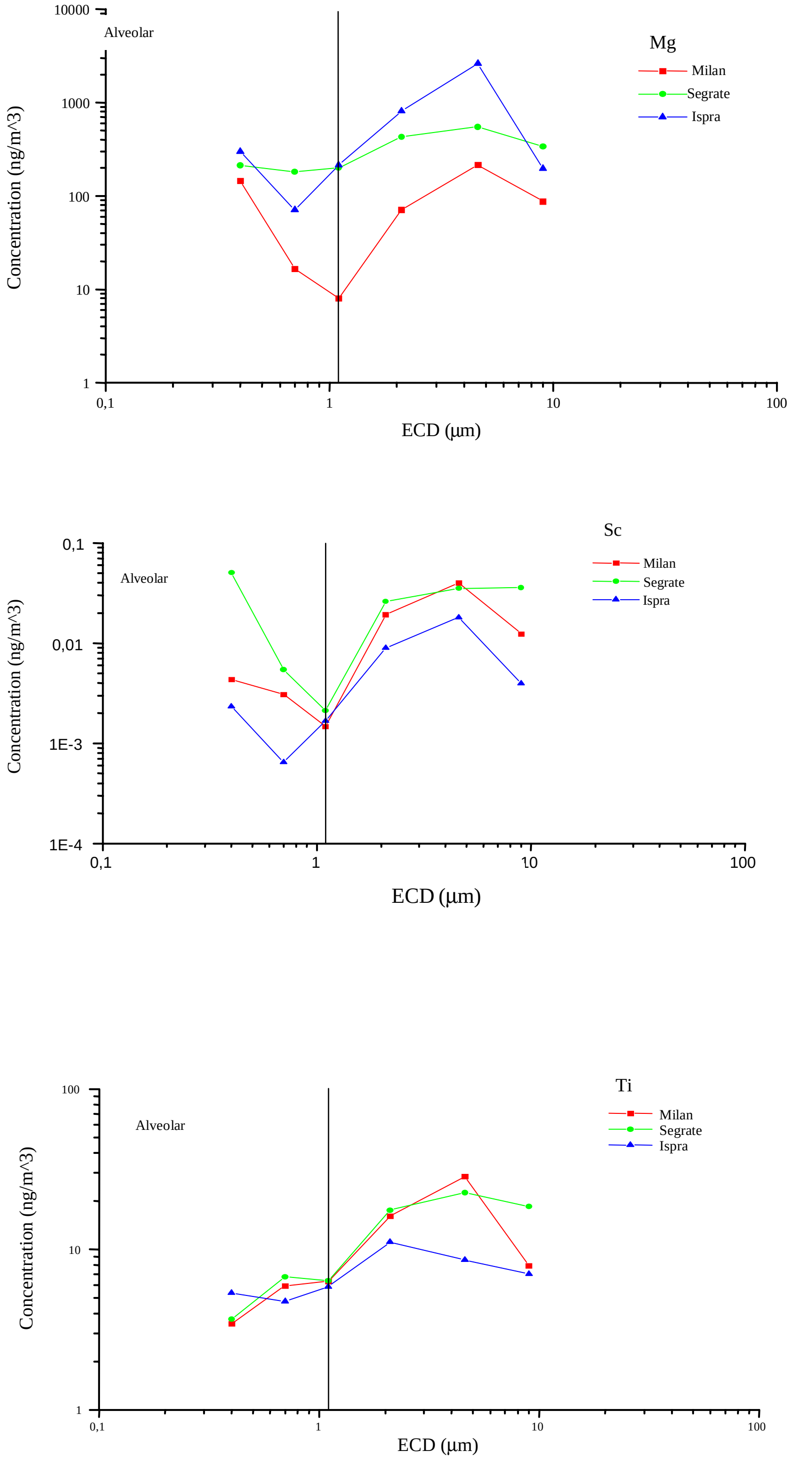


FIG. 2: Particle size distribution of some crustal elements (Mg, Sc, Ti) in the airborne particulate matter of urban, suburban-industrialised and rural residential areas of north Italy (summer 1998).

The overall data, obtained from the analyses of the size particles segregated fractions collected during the winter campaign, in the three locations, are summarised in Table 4 which reports the trace element percent distributions associated to the different human respiratory tracts.

TAB 4: Percent particle size distribution of 32 elements in the air particulate matter collected in the winter campaign (February '99).

	Milan				Segrate				Ispra			
Element	PM10	Alv.	Bronc.	Trach.	PM10	Alv.	Bronc.	Trach.	PM10	Alv.	Bronc.	Trach.
Ag	70-72	25	29	46	68-70	36	40	24	78-82	70	25	5
As	85-88	52	37	21	84-87	62	31	7	89-92	80	15	5
Au	78-82	40	33	27	75-80	40	30	30	75-80	61	32	7
Ba	85-89	5	48	47	70-75	23	63	8	80-85	67	26	7
Br	80-87	63	26	11	86-90	79	17	14	85-88	66	32	2
Cd	88-90	60	30	10	90-92	77	16	7	85-87	68	26	9
Ce	58-61	9	43	48	48-50	19	34	17	60-62	69	22	9
Cl	93-98	74	13	13	89-93	87	9	4	85-88	72	26	2
Co	77-80	30	45	25	75-77	70	20	10	62-65	67	19	14
Cr	88-93	14	54	32	90-93	35	49	16	86-88	50	37	13
Cs	55-58	48	22	30	60-65	48	15	37	70-75	36	54	10
Cu	85-90	15	60	25	72-75	19	61	20	75-80	57	30	13
Fe	72-74	4	60	36	50-52	12	72	16	75-77	13	59	28
Hf	71-75	14	70	16	56-60	27	59	14	-	-	-	-
Hg	92-95	42	28	30	90-95	50	23	22	90-92	42	17	41
I	93-95	65	19	16	83-88	67	24	9	95-97	77	18	5
K	70-74	52	23	25	70-75	61	23	16	72-74	60	33	7
La	49-51	10	41	49	41-45	21	15	64	72-74	47	25	28
Mg	50-55	5	37	58	50-53	8	49	43	60-63	8	70	22
Mn	74-78	17	50	33	75-78	47	41	12	68-70	48	41	11
Mo	85-90	15	54	31	87-90	38	58	4	75-77	85	12	3
Ni	78-80	50	30	20	71-75	61	27	12	82-85	67	18	14
Pb	70-72	57	30	16	76-79	70	23	7	78-82	69	25	6
Rb	28-30	15	47	38	56-60	36	32	32	50-56	40	31	29
Sb	86-88	14	61	25	85-88	30	61	9	86-88	50	40	10
Sc	48-51	6	39	55	42-44	14	54	32	65-68	10	49	41
Se	69-71	68	25	7	66-68	74	16	10	82-85	72	25	3
Th	54-56	8	57	35	46-48	34	30	36	43-45	30	26	44
Ti	65-70	14	40	46	62-66	14	52	34	80-83	38	27	35
V	80-84	51	28	21	80-85	66	25	9	88-90	68	24	8
W	80-85	39	29	32	80-85	60	30	20	-	-	-	-
Z	86-88	40	46	14	73-75	51	39	10	86-88	38	46	16

For each element are given the percentages associated to the “inhalable” fraction (PM10 fraction containing particles with an aerodynamic diameter AED of less than 10 μm) and the corresponding percentages in the subsequent finest “respirable” fractions (alveolar, bronchial and tracheo-pharynx).

TAB. 5: Percent particle size distribution of some elements in the air particulate matter collected in the summer campaign.

	Milan				**Segrate**				**Ispra**			
Elem.	**PM10**	**Alv.**	**Bronc**	**Trach**	**PM10**	**Alv.**	**Bronc**	**Trach**	**PM10**	**Alv.**	**Bronc**	**Trach**
As	35,4	78,6	15,9	5,5	80,4	97,2	1,4	1,4	90,4	81,0	14,3	4,7
Au	74,7	23,1	69,3	7,6	84,0	26,2	22,3	51,5	83,4	58,9	33,8	7,3
Br	68,3	60,8	29,2	10,0	93,2	56,7	24,5	18,8	89,6	67,5	25,1	7,5
Ce	41,4	63,2	14,5	22,3	92,7	18,1	30,7	51,2	-	35,7	30,8	33,6
Co	94,6	14,6	33,5	51,9	78,9	48,7	26,3	25,0	77,3	34,0	43,3	22,7
Cr	130,9	48,5	33,6	17,9	46,6	18,6	25,5	55,9	-	52,1	25,4	22,6
Fe	63,1	14,2	56,1	29,7	66,7	39,2	35,5	25,3	93,5	25,1	55,1	19,8
Hf	52,9	19,2	70,0	10,8	-	48,9	46,7	4,4	80,6	44,0	47,3	8,7
Hg	22,6	35,1	36,6	28,3	-	4,9	2,6	92,5	-	30,0	68,2	1,8
K	95,6	30,1	50,9	19,0	70,8	50.1	24,8	25,0	1,7	32,4	39,9	27,6
La	38,6	19,1	51,5	29,4	82,1	31,5	28,6	39,9	86,6	38,5	13,9	47,6
Mg	69,9	31,3	36,1	32,6	-	-	-	-	-	-	-	-
Mn	87,5	26,9	45,4	27,8	82,3	31,3	43,2	25,6	88,3	32,9	46,6	20,5
Mo	46,9	32,6	44,6	22,7	91,1	53,3	46,7	-	86,2	61,1	21,2	17,7
Rb	-	43,7	45,4	10,9	81,6	37,4	57,9	33,6	82,0	27,9	58,0	14,2
Sb	78,9	23,2	52,8	23,9	98,5	50,9	35,6	13,5	85,2	39,9	36,6	23,5
Sc	35,8	11,0	45,3	43,6	59,0	37,5	30,3	32,1	96,5	13,1	54,0	32,9
Sm	56,5	52,9	24,3	22,9	64,1	22,1	38,9	39,0	-	-	-	-
Th	45,1	22,1	43,8	34,2	77,0	39,6	42,5	17,9	98,2	32,1	34,9	33,0
Ti	89,9	23,0	47,8	29,1	97,3	22,3	40,9	36,9	-	-	-	-
V	72,4	66,5	21,4	12,1	78,1	58,3	23,5	18,3	-	-	-	-
Zn	73,4	61,0	20,8	18,2	98,1	40,0	40,4	19,6	89,0	49,7	46,4	3,8

The ranges of the percentage relative to the PM10 fraction were calculated as the ratio between the sum of the concentrations found in the 8 (or 9) fractions collected with the cascade impactors and those found in the analysis of the total air particulate collected meantime by the total air samplers. In all the three areas, the elements which may be considered of non anthropogenic origin and associated to natural sources (soils) such as Ce, Cs, La, Mg, Rb, Sc, and Th show the lower values in all the corresponding PM10 fractions. The great part of the other elements are present in the PM10 with high percentages suggesting that they are mainly associated to the fine “inhalable” particles released from polluting sources (combustion, chemical processes etc.). Among these elements, Pb, Ni, Sb and Br which are related to the automotive emissions show in all three PM10 fractions comparable percentages confirming their common origin. The main interesting data however, are those regarding the percentages measured in the finest fractions where the values may sensibly differ. Here many elements of toxicological interest show relative high percentages in the alveolar fraction which, being more deeply inhaled into the lungs, may increase the risk of disease through exposure. In this contest, it may be observed that, for many of these elements, the percentages found in the alveolar fraction of Ispra are higher in comparison with those of Milan and Segrate. This may be explained with the arrival into the “unpolluted” area of Ispra of the finest particles, mobilised by long distance transport from the far pollutant emission points.

These same results can be observed in Table 5 in which the data of the summer campaign are presented. It can be noticed that for all the elements, of anthropogenic origin, the concentrations in the winter campaign are greater than those obtained during the summer campaign, especially for the total concentration. During winter time, in fact, the greatest atmospheric pollution phenomena take place (thermal inversion, condensation, fog, etc.), because of both worse climatic conditions and domestic heating.

5 CONCLUSIONS

The INAA was found highly sensitive and reliable for both multielemental determination in the samples and the analytical control of the blanks. Its use in this type of studies allows the analysis of many elements at the few nanogram levels. The blank contribution from the filters constitutes the major source of error especially when the concentrations are very low and small amounts of air dust are collected. A very accurate analysis of the filtering material must be carried out to obtain reliable blank values for appropriate corrections of the final results.

The errors here reported are obtained as the mean standard error of the measures realised. As a matter of fact it is extremely difficult to evaluate an absolute error because of many reasons. First of all element content on the blanks is very often found to be greater than that found on the samples. Moreover since the sampling technique is very long and the weather conditions are not always reproducible the number of samples collected is poor and different. Finally the statistics itself is not sophisticated because counting statistics, especially for short living isotopes, is not so good. So every rigorous statistic treating would be a nonsense.

By the study of the granulometric distribution we can conclude that the greatest part of potential toxic elements are associated with fine particulate, that is present even in “clean” areas because of long distance transport phenomena.

At the end of this work we realised that, in order to give a theoretic better interpretation of data, we need a suitable model which studies the distribution of particle matter in the different compartments of our respiratory system, as the ICRP model, already developed (ICRP 66), is good to explain radioactive material intake, but it seems not completely good to treat particle matter deposition.

6 ACKNOWLEDGEMENTS

This work was carried out with the financial support of the National Institute of Nuclear Physics (INFN), the University of Milano and CNR of Pavia, Italy. The neutron irradiations of the samples were carried out at the TRIGA Mark II (General Atomic – USA) research nuclear reactor of the University of Pavia, Italy.

7 REFERENCES

(1) W. Schroeder, et al., Toxic Trace Elements Associated with Airborne Particulate Matter: a Review. J. Air Poll. Control Ass. (JAPCA), **37**, 1267 (1987).
(2) Who/UNEP, 1992 Urban air Pollution in Megacities of the World. World Health Organisation, U. N. Env. Prog., Blackwell, Oxford, (1992).
(3) M. Gallorini, et al., Trace elements content in the respirable fractions of the air particulatemof urban and rural areas monitored by neutron activation analysis. In Publishing in Biol. Trace Elements.
(4) E. Rizzio, et al., The Science of the Total Environment, **226**, 47, (1999).
(5) R. Dams, Pure & Appl. Chem., **64 n. 7**, 991, (1992).
(6) Alian and B. Sansoni, "Activation Analysis in Air Particulate Matter", in Zeev B. Alfassi (ED) Activation Analysis, vol **II**, CRC Press Inc., Boca Raton, 503, (1990).
(7) S. Landsberger, et al., J. Radioanal. Nucl. Chem., **217** n.1, 11, 1997).
(8) R. Zeisler, et al., J. Radioanal. Nucl. Chem., **217 n. 1**, 5, (1997).
(9) M. Gallorini, Microchemical J. **51**, 127, (1995).
(10) E. Rizzio, et al., Trace elements in total and in respirable fractions of air particulate investigated by neutron activation analysis. Proc. XI National Congress “Research Activities in Radiochemistry, Radiation Chemistry, Nuclear and Radioelements Chemistry”. Rome 1998.
(11) Ranz, W. E., and J. B. Wong, "Jet Impactors for Determining the Particles Size Distribution of Aerosols", Arch. Ind. Hyg. Occup. Med. **5**, 464, (1952).
(12) M. Gallorini, et al , J. Rad. Nucl. Chem., **35** Nos 1-2, 241, (1998).