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RESEARCH ARTICLE

Studies on The Appropriate Type of Filter Sampling to Analyze The Atmospheric Trace Element Using Three Analytical Methods

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Abstract

Different atmospheric aerosol samples were collected on three types of filters. Different disks were cut and investigated by XRF, PIXE and scanning electron microscopy (SEM) for both the loaded and clean areas. In PIXE, both blank and aerosol samples were bombarded with 2 Mev proton from 5 Mv Van de Graff accelerator in the Institute of Nuclear Research, (Debrcen, Hungary). The blank concentration values of the elements. Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br and Pb in the three types of filter are discussed. It is found that for trace elemental analysis, the Nuclepore membrane filters are the most suitable for sampling. These filters have much lower blank element concentrations than the glass fiber and ash free filters. It was also found that PIXE is a more reliable analytical technique for atmospheric aerosol particles than the other methods used.

Introduction:-

An important factor in obtaining a useful aerosol sample is the collected material. The filter should be retentive for particles but must be permeable for air flow. It should provide the aerosol sample ready to quantify both the total mass of the collected material and the chemical composition of the sample. Although these conditions seem to be self-evident, there are several inherent and un resolvable conflicts in these requirements different types of filters such as glass fiber, ash free and membrane filters have been used for many years in trace elemental sampling. Glass fiber filters and "Hi-Vol" samplers have been used for more than 50 years to measure and control air pollution. Standard methods for routine chemical analysis of particulate matter on glass fiber filter were established, and are still used by many air pollution control agencies Refs [1-4].

H. E. Nustadter et al.[5] found that cellulose filter materials, could be employed in ambient monitoring with insignificantly lower collected mass if proper care were taken for the humidity equilibration that must be respected before taking exposed or unexposed filter weights. Paper filters have been found to have somewhat lower retention when sampling begins[6] but their collection capability will improve as the loading of particles begins to develop.[7] They have a high loading capacity and have low blank values.[8]

Nuclepore filter consists of thin polycarbonate sheets with fine capillary pores, and in contrast to classical membrane filters, Nuclepore filters have a uniform structure and pore-size distribution, A general characteristic of membrane filters, and particularly of Nuclepore filters, is that the aerosol particles are collected on or close to the surface of the filter than in the case of fibrous filters. Consequently, for X-ray emission techniques such as XRF and PIXE, where absorption of the incident radiation and/or the generated characteristic X-rays have to be considered, membrane filters have definite advantages over fibrous filters.

In the present paper a systematic study of the applicability of three types of filters for XRF, PIXE and SEM has been carried out, to find which elements can or cannot be analyzed on a special type of filter in the next section. The results and discussion are presented in section 3. The conclusion is outlined in section 4.

Experimental:-

The atmospheric aerosol samples were collected separately during different periods on three different of filters; glass fiber, ash free and membrane filters with air volumes of 200-300, 1-2 and 10-12m^3, respectively. The filter materials can be characterized as follows:

(1) Smooth and rough glass fiber prefilter; Sartorius SM 134 00, and Paraplan filter. The diameter of the filter was 257 mm and the loaded area was 230 mm in diameter;

(2) Ash free filters, type MN 640 m. The diameter of the filters was 50 mm and the exposed area was 40 mm in diameter;

(3) Nuclepore membrane filters, BA85/21, pore size 0.45 µm. The diameter of the filter was 50 mm and the exposed area was 40 mm in diameter.

Disks cut from both blank and loaded areas of each kind of filters were investigated with three analytical methods. In PIXE, both the blank and the aerosol samples were bombarded with 2 MeV protons from the 5 MV Van de Graff accelerator in the Institute of Nuclear Research. The calibration of the PIXE setup used for exciting and detecting the X-ray spectra has been described in ref.[9] The measurement period for the atmospheric aerosol samples were 1000 seconds (^{125}I) and 300 seconds (^{55}Fe), respectively. Some electron micrographs were taken of the blank and loaded filters by a SEM (type – AMRAY 1830 l USA). All the samples were coated with a thin layer of gold.

All the spectra were analyzed by the PIXYKLM program.[10] The analyses with XRF were carried out with an automatic measuring XRF system basedon an ATOMKI-type Si(Li) at Mn K line. The X-ray lines of a ring shaped ^{125}I (200 MBq activity) source and ^{55}Fe (26 GBq) source were used for the excitation of low atomic number elements (Si, S, Cl, K, Ca, Ti, V, Cr) while the ^{125}I source was used for those of high atomic number (Z > 24).[13]

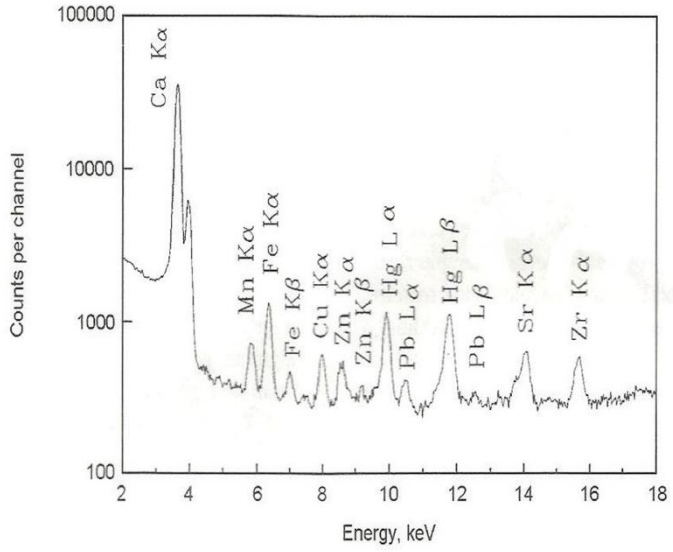

Fig .1. Atypical X-ray spectrum (XRF) for glass fiber filter

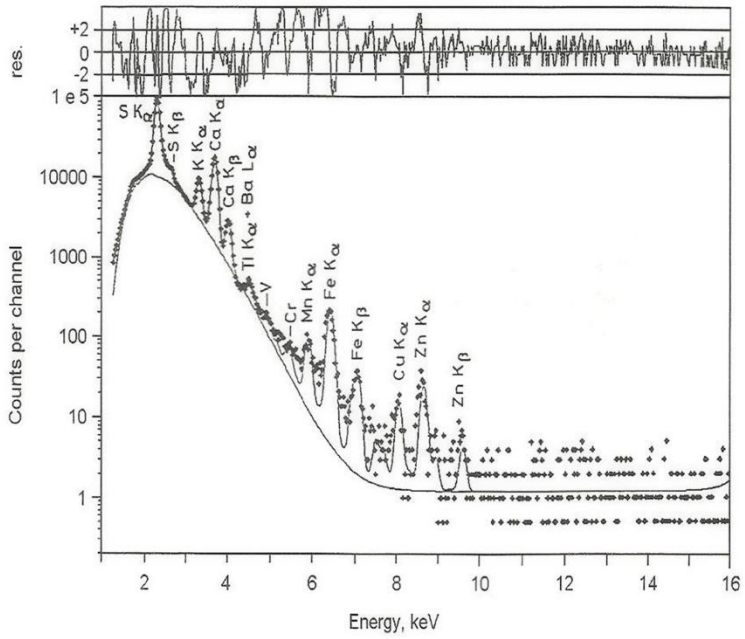

Fig .2. Atypical PIXE spectrum for blank membrane filter

Results and discussion:-

In order to get reliable analytical results, the elemental composition of the blank filters has been investigated before sampling. Elements present in high concentration in the filter material may overlap with the weak micro elemental components in the samples to be measured. Such events may spoil the inherent sensitivity of the elaborated analytical methods. The applicability of the Sartorius and Paraplan glass fiber filters, in XRF analysis has been studied. A typical spectrum of XRF for glass fiber can be seen in Fig. 1. The average concentration value of 50 independent measurements of characteristic X-ray peak counts of aerosol samples and blanks are reported with their standard deviation in Table 1.

Elements having significantly higher characteristic peak intensities in the sample than in the blank area are regarded as measurable ones. For the determination of significant differences between the blank and samples, the unpaired T-test was used. It can be seen, that selecting $p<0.001$ significance level, only the S and Pb elements are measurable from the 24 elements analyzed. The blank glass fiber filter contains almost all of the element to be measured.

These results show, in accordance with other literature data, ref. [14, 15] that the blank glass fiber filters have very high values of element analysis of aerosol samples. Quantitative trace element determination in glass fiber is rather thick and the depth profile of mass deposition for various particles in unknown. Finally, we can conclude that PIXE is unsuitable for trace element analysis of aerosol samples collected on glass fiber filters.

Table .1. Blank and loaded glass fiber filters (tow different types, Sartorius and Paraplan) analyzed by XRF

Element	Sample Mean ± S.D.		Blank Mean ± S.D.		T-stat	p
Sartorius						
Si	14392	250	15302	440	-4.0	0.004*
P	161	67	88	89	1.5	0.178
S	427	78	166	30	7.0	0.000*
Cl	514	112	387	29	2.5	0.039*
K	29584	342	30517	1339	-1.5	0.169
Ca	30985	2037	28955	2014	1.6	0.152
Ti	9234	2869	13472	6625	-1.3	0.226
Ba	65069	2854	64004	10133	0.2	0.827
Mn	211	28	198	11	0.9	0.372
Fe	591	160	352	54	3.2	0.013*
Co	39	29	57	22	-1.1	0.304
Ni	110	24	94	36	0.8	0.453
Cu	258	40	260	49	-0.1	0.923
Zn	47279	793	46480	327	2.1	0.071
Se	13	11	1	13	1.8	0.111
Br	46	20	45	13	0.1	0.927
Rb	798	41	821	55	-0.8	0.463
Sr	2916	85	2859	70	1.1	0.287
Zr	259	30	227	22	2.0	0.085
Mo	39	13	45	25	-0.5	0.649
Cd	14	21	2	56	-0.6	0.576
Au	73	39	88	31	-0.7	0.526
Hg	3	24	1	14	0.2	0.865
Pb	289	23	138	32	8.6	0.000*
Paraplan						
Si	19565	385	20333	225	-3.9	0.005*
P	493	68	511	49	-0.5	0.643
S	1249	77	376	32	23.4	0.000*
Cl	177	33	266	24	-4.9	0.001*
K	11133	192	10734	136	3.8	0.005*
Ca	110905	1249	112860	819	-2.9	0.019*
Ti	641	168	576	128	0.7	0.509
Ba	1531	61	1646	157	-1.5	0.163
Mn	26	25	15	28	0.6	0.557
Fe	431	46	437	32	-0.2	0.829
Co	18	23	7	10	1.0	0.357
Ni	40	12	35	25	0.4	0.681
Cu	62	30	21	10	2.9	0.019*
Zn	1147	49	1074	61	2.1	0.071
Se	10	39	13	11	-0.2	0.872
Br	81	26	31	43	2.2	0.060
Rb	78	33	74	23	0.2	0.814
Sr	233	27	209	23	1.6	0.156
Zr	362	45	344	17	0.8	0.434
Mo	56	20	40	36	0.9	0.397
Cd	3	12	1	38	0.1	0.930
Au	75	20	67	26	0.6	0.562
Hg	17	12	22	19	-0.4	0.691
Pb	236	19	139	28	6.4	0.000*

Table .2. Elemental concentration values for blank and loaded membrane filters analyzed PIXE

Element	Area	Error	SLA	Concentration, ppm	Error	SLC
Blank						
Si	2185.0	± 433.9	1003.6	2.910E-02	±6.438E-03	1.337E-02
S	461165.9	±876.9	1290.6	2.724E+00	±1.100E-01	7.623E-03
Cl	28504.8	± 604.7	1350.8	1.512E-01	±7.041E-03	7.167E-03
K	34824.6	± 364.5	728.4	2.027E-01	±8.501E-03	4.240E-03
Ca	93265.0	±385.2	546.2	6.197E-01	± 2.516E-02	3.630E-03
Ti	814.0	±101.8	227.3	8.550E-03	±1.221E-03	2.387E-03
V	184.8	± 70.0	159.8	2.442E-03	±1.018E-03	2.111E-03
Cr	868.9	± 41.9	89.8	4.330E-03	±7.602E-04	1.446E-03
Mn	484.8	± 33.6	59.0	9.986E-03	±8.584E-04	1.216E-03
Fe	1337.6	± 40.3	39.6	3.434E-02	±1.791E-03	1.018E-03
Co	113.6	± 20.9	41.7	3.792E-03	±7.781E-04	1.393E-03
Ni	22.8	± 9.7	19.6	9.409E-04	±4.395E-04	8.092E-04
Cu	92.3	±11.9	16.4	5.111E-03	± 7.522E-04	9.105E-04
Zn	149.6	± 13.8	14.8	1.064E-02	± 1.156E-03	1.050E-03
Ba	616.6	± 107.0	242.2	2.655E-02	± 5.160E-03	1.043E-02
Sample						
Al	9192.1	± 355.6	796.6	4.106E-01	± 2.386E 02	3.559E-02
Si	171338	± 646.0	1153.9	2.252E-00	± 9.132E 02	1.517E-02
P	77489.7	± 687.2	1461.6	5.970E-01	± 2.475E 02	1.126E-02
S	481514.3	± 911.9	1376.5	2.807E+00	± 1.134E 01	8.025E-03
Cl	26600.6	±620.3	1392.2	1.393E+01	± 6.626E 03	7.290E-03
K	156643.1	± 516.2	771.1	9.000E-01	± 3.645E 02	4.430E-03
Ca	297078.6	± 633.5	751.0	1.948E-00	± 7.872E 02	4.925E-03
Ti	8582.9	± 149.7	273.6	8.899E-02	± 3.963E 03	2.837E-03
V	1023.9	± 101.0	222.9	1.335E-02	± 1.522E 03	2.906E-03
Cr	785.5	± 70.3	149.9	1.249E-02	± 1.308E 03	2.383E-03
Mn	3041.4	± 83.6	146.1	6.183E-02	± 3.098E 03	2.971E-03
Fe	56122.2	± 240.1	90.9	1.422E-00	± 5.774E 02	2.303E-03
Co	834.8	±112.2	252.3	2.750E+02	± 4.149E 03	8.313E-03
Ni	261.8	± 30.1	59.2	1.066E-02	± 1.395E 03	2.409E-03
Cu	351.7	± 24.2	35.6	1.922E-02	± 1.627E 03	1.945E-03
Zn	2255.1	± 48.7	25.1	1.584E-01	± 7.382E 03	1.765E-03
Br	63.2	± 12.3	21.7	1.762E-02	± 3.759E 03	6.044E-03
Ba	211.1	± 178.1	412.9	8.971E-03	± 8.190E 03	1.755E-02
Pb	257.9	± 19.9	27.4	1.291E-01	± 1.198E 02	1.374E-02

SLA and SLC : Standard limit area, and standard limit concentrations, respectively

The ash free filter of Mn 640m type was also investigated by XRF. It was found that this type of filter has lower blank concentration values than the glass fibre filters and it is suitable for the quantitative analysis of trace elements Al, S, K, Ca, Ti, Br, Ba and Pb. On the other hand, it is considered much more suitable for aerosol samples taken from car exhaust gas than for other type of samples, because it is blank are free from Br and Pb.[16]

PIXE was used to investigate the Nuclepore membrane filters, which were found to be superior to the above sets of filters. A typical spectrum for a blank membrane filter can be seen in Fig.2. The elemental concentration values for blank and loaded membrane filters that analyzed by PIXE are summarized in Table2. It can be seen that membrane filters have much lower blank concentration values than those present in the aerosol samples. The membrane filters

are much suitable for measuring the concentration of the trace elements Al, Si, s, Cl, K, Ca, Ti, V, Fe, Cu, Br, Ba and Pb for atmospheric aerosol samples.

For trace elemental analysis, it is more common to collect the samples on membrane filters that provide samples better suited for PIXE analysis.[17] The collection efficiency depends on the pore size, particularly for the Nuclepore filters. JOHN and REISCHI,[18] found that 0.8 µm Nuclepore filters have only a 72% efficiency for sub-micron particles detectable with a condensation nuclei counter. It contrast, 0.4 µm and 0.45 µm Nuclepore filters are more than 99.9% efficient under the same experimental conditions.

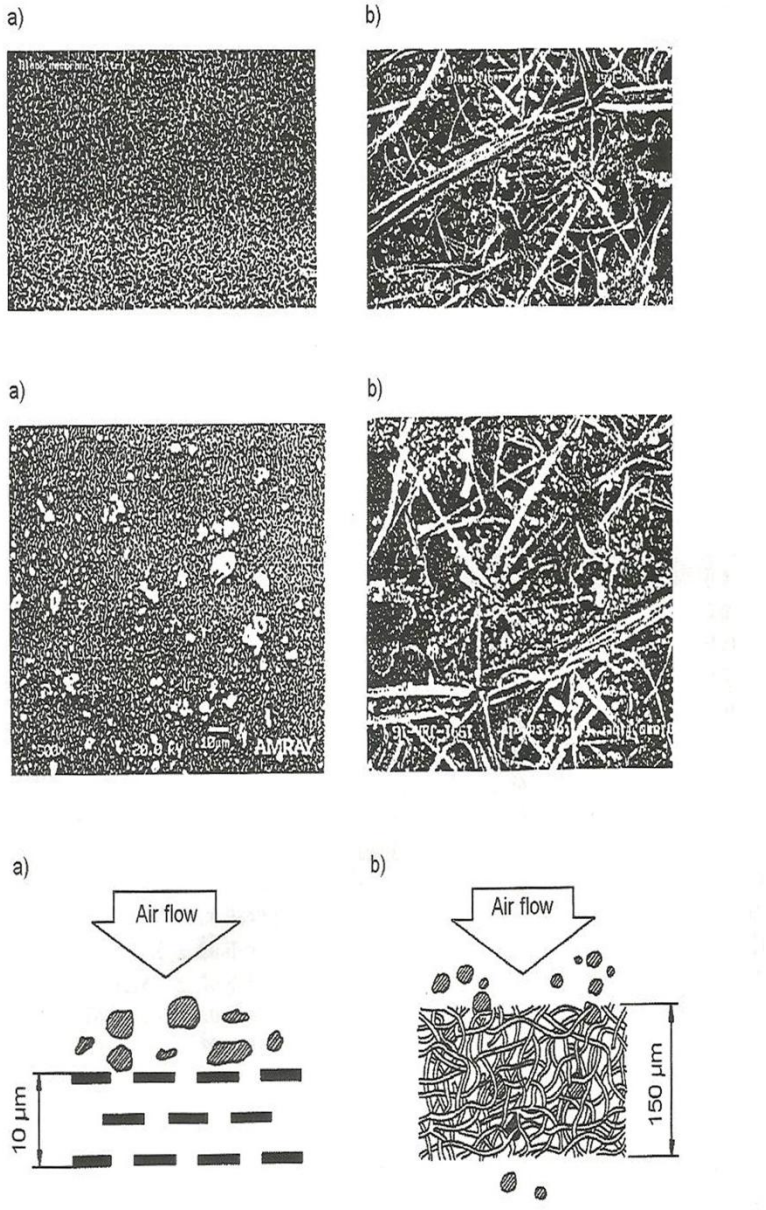

Fig. 3. Electron micrographs for blank (a) and loaded (b) filters taken by a scanning electron microscope

Some electron micrographs for blank and loaded filters taken by SEM are shown in Fig. 3. The micrographs support the conclusion that in the case of membrane filters the surface filtering effect and the thin filter material secure conditions for the filtration than the conditions of glass fiber filters characterized by depth filtering and a thick

filtering layer. In the former case one ends up with a thin surface layer of deposited material and insignificant filter mass, contributing only with a weak background in the X-ray spectroscopy. In the latter case, however, we have a distributed in-depth layer of the deposit covering the whole surface of the filter with a significant mass.

In PIXE the energy straggling of the bombarding charged particles will be decreased in the case of membrane filters. X-ray absorption of lower lying layers which can be considerable in the case of fibrous filters, will be practically absent. Due to the thin filter structure, the background will be decreased with respect to thick filters as well. To compare the three types of filter materials, the average blank concentration values obtained by different methods are presented in Table 3 It can be seen, that the glass fiber filters have blank concentration values about 30 times higher than the ash free filter and about 50 times higher than the membrane filters. This means, that the glass fiber filter is quite unsuitable for trace element samples. It is much better to use the membrane filters for atmospheric aerosol particle analysis.

Table.3. Average blank concentration values (in Mg/m^3) of some element in three different of filters

Element	Glass fiber filter ED-XRF	Ash free filter ED-XRF	Membrane filter PIXE
Al	–	–	–
Si	178	1.56	0.029
S	3.76	0.59	2.72
Cl	1.48	2.07	0.15
K	37.26	0.32	0.20
Ca	20.61	0.70	0.62
Ti	10.71	–	0.01
V	8.78	–	0.002
Fe	2.96	2.05	0.034
Cu	1.35	–	–
Br	0.37	–	–
Ba	66.23	0.05	0.02
Pb	0.61	0.40	–

Conclusions:-

The atmospheric aerosol particles were collected on three different types of filters. XRF, PIXE and SEM were used for elemental concentration analysis. It was found that the blank glass fiber filter contains almost all of the element to be measured, such as Si, S, Cl, K, Ca, Ti, Ba, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Zr and Mo. Quantitative trace

element determination in glass fiber filters by PIXE is complicated because the filter is rather thick and the depth profile of mass deposition for various particles is unknown. The membrane filter have much lower blank element concentration values than the aerosol have. The glass fiber filter is quite unsuitable for atmospheric trace element analysis by X-ray spectroscopy and it is much better to use Nuclepore membrane filters for samples to be analyzed preferably by PIXE.

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