

This article was downloaded by:

On: 17 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

### Application of Ion Chromatography, Nuclear and Spectrochemical Techniques for Trace and Major Element Determination in Seaside Aerosols

Duran Karakas<sup>a</sup>; Ilhan Olmez<sup>b</sup>; Gurdal Tuncel<sup>c</sup>

<sup>a</sup> Chemistry Department, Middle East Technical University, Ankara, Turkey <sup>b</sup> Nuclear Reactor Laboratory, Massachusetts Institute of Technology, Cambridge, MA, USA <sup>c</sup> Environmental Engineering Department, Middle East Technical University, Ankara, Turkey

Online publication date: 17 September 2010

**To cite this Article** Karakas, Duran , Olmez, Ilhan and Tuncel, Gurdal(2002) 'Application of Ion Chromatography, Nuclear and Spectrochemical Techniques for Trace and Major Element Determination in Seaside Aerosols', *International Journal of Environmental Analytical Chemistry*, 82: 10, 705 – 720

**To link to this Article:** DOI: 10.1080/0306731021000075429

**URL:** <http://dx.doi.org/10.1080/0306731021000075429>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# APPLICATION OF ION CHROMATOGRAPHY, NUCLEAR AND SPECTROCHEMICAL TECHNIQUES FOR TRACE AND MAJOR ELEMENT DETERMINATION IN SEASIDE AEROSOLS

DURAN KARAKAS<sup>a,\*</sup>, ILHAN OLMEZ<sup>b</sup> and GURDAL TUNCEL<sup>c</sup>

<sup>a</sup>*Chemistry Department, Middle East Technical University, 06531 Ankara, Turkey;*

<sup>b</sup>*Nuclear Reactor Laboratory, Massachusetts Institute of Technology, Cambridge,  
MA 02139-4307 USA;* <sup>c</sup>*Environmental Engineering Department,  
Middle East Technical University, 06531 Ankara, Turkey*

*(Received 16 August 2001; In final form 14 March 2002)*

Instrumental neutron activation analysis, flame atomic absorption spectrometry, flame atomic emission spectrometry, graphite furnace atomic absorption spectrometry, ion chromatography and visible spectrometry were applied to determine the compositions of atmospheric aerosols, which were collected at a rural site in the Western Black Sea Coast of Turkey. A total of 354 daily aerosol samples were analyzed for about 46 trace and major elements and ions. Sample preparation, quality control procedures, and instrumental operating conditions were reported. Most of the elements measured commonly by the above techniques have very large correlation coefficients and low intercept values indicating the agreement between the results.

*Keywords:* FAAS; FAES; GFAAS; IC; INAA; Coastal aerosol

## INTRODUCTION

Aerosol samples at rural sites contain very low concentrations of heavy elements and requires highly sensitive analytical methods, great precautions during sampling, conservation and manipulation of the samples in order to avoid both losses and contamination of elements. Deducing a high number of parameters determined from an environmental sample is very important for determining the sources and transport mechanisms of the pollutants. Trace and major elements determined in environmental samples are generally used as markers for the emission sources, and therefore, the great number of marker elements are very useful in environmental studies. In order to get large numbers of markers, multielement analytical techniques and/or more than one analytical technique is required. Commonly used analytical techniques for the

---

\*Corresponding author. Present address: TUBITAK-Marmara Research Center, Earth and Marine Sciences Research Institute, P.O. Box 21, 41470 Gebze/Kocaeli/Turkey. Fax: +90-262-641 2309. E-mail: Duran.Karakas@posta.mam.gov.tr

determination of sample compositions at very low concentrations in atmospheric aerosols and wet-dry depositions are Graphite Furnace Atomic Absorption Spectrometry (GFAAS) [1–7,18], Instrumental Neutron Activation Analysis (INAA) [3,5,8–11,20], Proton Induced X-Ray Emission (PIXE) [12–16], Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) [17,18,21,22,31], Stripping Voltammetry [18], Electron-probe X-ray Microanalysis (EPXMA) [19,23–25,27], Aerosol Time-of-Flight Mass Spectrometers (ATOFMS) [26,28] and X-Ray Fluorescence techniques (Total Reflection X-Ray Fluorescence [30], Wavelength Dispersive X-Ray Fluorescence [29], Energy Dispersive X-Ray Fluorescence [31]).

In this study, the aerosol samples were analyzed for trace and major elements by using Instrumental Neutron Activation Analysis (INAA), Graphite Furnace Atomic Absorption Spectrometry (GFAAS), Flame Atomic Absorption Spectrometry (FAAS), Flame Atomic Emission Spectrometry (FAES), Ion Chromatography (IC) and Visible Spectrophotometry (VIS). Sample collection and preparation for the analyses and the results obtained from analytical techniques were compared and discussed. Interpretation of obtained data for environmental point of view will be discussed in subsequent publications.

## EXPERIMENTAL

### Sampling Site and Sample Collection

An atmospheric sampling and pollution monitoring station was implemented at the Western Black Sea Coast of Turkey in 1995. The station is located 20 km east of Amasra town (Fig. 1) and 3.5 kms south/southwest of the Black Sea Coast ( $41^{\circ}47' N$  and  $32^{\circ}29' E$ ). The altitude of the station is approximately 150 m. The station consists of a platform, where a Hi-Vol PM-10 aerosol sampler and a wet-and-dry deposition collector were located and a field laboratory, which contains sulfur dioxide, nitrogen

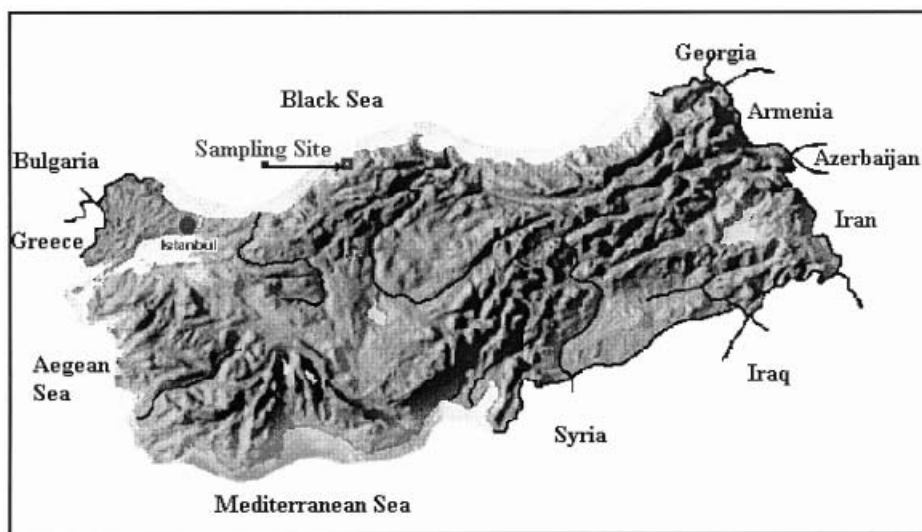


FIGURE 1 Location of sampling site.

oxides (NO and NO<sub>2</sub>), ozone, PM-10 suspended particulate matter (SPM) monitors and a recording rain gauge. The field laboratory also served as a clean space to change samples, storage area for collected samples, spare parts and power distribution center. The sample change area consisted of a table, for which precautions were taken to minimize sample contamination during filter-changes. The table was lined with a sheet of polyethylene and a small plate of Plexiglas was placed on the polyethylene sheet. The Plexiglas was first wiped with a damp, then with a dry cleanex, before filters were processed every day. The plate was covered with nylon bags, when it was not used.

Aerosol samples were collected using a Sierra-Andersen Model SAUV-10H PM-10 High Volume sampler on 20.3 × 25.5 cm Whatman 41 cellulose filters. A size selective inlet, attached to the Hi-Vol sampler, removed particles > 10 μm aerodynamic diameter before they entered to the sampling system. Particles with sizes less than 10 μm were collected on the filter, and the larger particles were precipitated on the collection shim of the inlet, or pre-impacted before reaching to the nozzles. The larger particles collected in the impaction chamber on the collection shim were removed during maintenance periods. Sampling flow rates varied between 1.4 and 1.7 m<sup>3</sup> min<sup>-1</sup>.

### Instrumentation

In this study, 354 daily aerosol samples, which had been collected from the Black Sea atmosphere between 1995 and 1997, were analyzed for approximately 46 species by the application of FAAS, FAES, GFAAS, INAA, VIS and IC. Lead, Ni, Cr, Cd and V were determined by GFAAS using a Perkin Elmer Model 1100B Spectrometer equipped with a HGA 700 graphite furnace electrothermal atomizer. High purity Argon gas used was purchased from BOS (Birleşik Oksijen Sanayi A.Ş.) and the purity of Ar gas was 99.998%.

Aluminum, Mg, Fe, Zn, Cu and Ca were determined by Flame Atomic Absorption Spectrometry (Perkin Elmer 1100B Spectrometer with Air/Acetylene (BOS, 98.5% min purity) and Nitrous oxide (BOS, 99.0% min purity)/Acetylene flame for Al). Sodium and K were determined by Flame Atomic Emission Spectrometry. The Na, Mg, Al, Ca, Cl, K, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Mo, Cd, In, Sb, Ba, Cs, La, Ce, Sm, Nd, Yb, Lu, Hf, Au, Th, U and Hg were determined by INAA. For INAA, samples were irradiated at the Massachusetts Institute of Technology (MIT), MITR II Research Reactor at a neutron flux of  $8 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ . The major anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were determined by IC (Varian model 2010 HPLC coupled to a JASCO UV/VIS 875 detector). The IC system was connected to a personal computer (PC) and PEAK2 software was used to run the system. The ammonium ion in the aerosol was determined by VIS Spectrophotometry (UNICAM 8625 UV/VIS Spectrometer) with Nessler's method.

### Preparation of Samples for Spectrochemical (FAAS, FAES, GFAAS) analysis

Sample and field blank filters were weighed and divided into four parts. The first part was used for IC analyses and the second and third quarters were used for AAS and INAA analyses, respectively. The last quarter was stored for future use. Samples were digested before the analysis by AAS. For the digestion and handling of aerosol loaded filter samples for AAS analyses, procedures developed in the WMO/UNEP

Expert Meeting on Quality Assurance for the MEDPOL Airborne Pollution Measurements (27–30 May, 1993) were slightly modified and used. One fourth of the aerosol filters were transferred into 250 mL Teflon beakers and 40 mL subboiled nitric acid (HNO<sub>3</sub>) (analytical grade Nitric Acid, MERCK, 65% pure was used to prepare subboiled reagent) was added. Teflon lids were placed on beakers and the samples were refluxed for 12–14 h on a hot plate at 140 ± 10°C. In each set, 18 aerosol samples, 1 acid blank and 1 filter blank were simultaneously prepared. The clearness of the filter blank after reflux showed the complete dissolution of the sample. If there were undissolved filter material, 10 mL of additional nitric acid (HNO<sub>3</sub>) was added to each of the samples, and refluxed for 4–6 h to complete the dissolution. At the end of this period, covers were removed and the aliquots were evaporated until approximately 1–2 mL sample solution was left. Then 5 mL “supra pure” hydrofluoric acid (HF, commercial suprapure grade, MERCK) was added to each sample including acid and filter blanks. The beakers were again covered with their lids and refluxed for another 6–8 h. The HF was added to dissolve alumina-silicate matrix, which exists in the samples due to presence of crustal particles. When the dissolution was completed, the lids were removed and the solutions were evaporated near dryness. Nitric acid (5 mL) was added to each beaker and solution was evaporated in order to remove all the HF from the solution. This step was repeated until no white HF fume was observed. Complete evaporation of HF is essential, because the HF remaining in the sample solutions can cause serious damage of the glass, and quartz components of the spectrometers, when aspirating (nebulizing) solutions of such types for measurements. After evaporating all of the HF, samples were removed from the hot plate, cooled and diluted to 50 mL with 1(m/m)% subboiled HNO<sub>3</sub> solution.

### Preparation of Samples for INAA

For INAA, approximately one sixteenth of the sample filter was irradiated twice in the 4.9 MW MITR-II research reactor at a neutron flux of  $8 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ . For the determination of short-lived isotopes, Al, Mg, Ti and V, samples were irradiated for 1 min and immediately counted with high purity germanium detectors for 7 min. At the end of this “Short-1 count”, samples were recounted for 20 min to determine the gamma ray activities of the isotopes with half-lives in the range of 37.3 min (Cl) to 15 h (Na). These isotopes were Na, K, Cl, Mn, In, Ba and Yb. Samples were then allowed to decay for about three weeks, and the cooled samples were reirradiated for 6 h, and counted for 6–10 h for the determination of the activities of the long lived isotopes (Ca, Sc, Cr, Fe, Co, Zn, As, Se, Br, Mo, Cd, Sb, Cs, La, Ce, Sm, Nd, Hf, Au, Th, U and Hg). Gamma-ray emitted from the irradiated samples were collected using high-purity-germanium (HPGe) detectors coupled to a 8192-channel pulse-height analyzers (Cannberra, CT). Collected spectra were analyzed using software ND 9900 Genie System run on VMS 200, Cannberra, CT. Masses of elements were determined by comparing activities of the elements in the sample with those in standards (SRM-1633, Coal Flyash). Masses of the elements were first corrected for the field blanks and divided by the sample air volume corresponding to the one-sixteenth of the aerosol filter samples, and the final results were expressed in  $\text{ng m}^{-3}$ . Accuracy of the analytical method was checked by analyzing NIST SRM-1571 (Orchard Leaves) which was irradiated and counted along with the samples and standards.

### Preparation of Samples for IC and VIS Spectrophotometry

For IC analyses, one-fourth of each filter was placed into a 100 mL glass beaker containing 50 mL of doubly distilled deionized water. The beaker was placed into an ultrasonic shaker and sonicated for 40 min. The extract was filtered through 0.22  $\mu\text{m}$  pore size cellulose acetate membrane filter and an aliquot of 100  $\mu\text{L}$  from the filtrate was injected to the IC. The mobile phase was 1.0 mM phthalic acid, buffered to pH of 4.95 with the addition of saturated sodium tetraborate (prepared from analytical grade reagent, MERCK) solution. The mobile phase was degassed for approximately 30 min to purge the dissolved air. Calibration curves were prepared with 0.50, 1.00, 3.00, 5.00, 10.00 and 15.00 ppm (mg anion/L solution) standard solutions of  $\text{Cl}^-$  (from NaCl, Merck),  $\text{NO}_3^-$  (from  $\text{NaNO}_3$ , Merck), and  $\text{SO}_4^{2-}$  (from  $\text{K}_2\text{SO}_4$ , Merck).

Ammonium ion concentration was determined in the same sample solutions as prepared for the IC analyses. For this purpose, the so called "direct Nesslerization" method was applied. In this method, Nessler's reagent which is an alkaline solution of mercury iodide ( $\text{K}_2\text{HgI}_4$ ) reacts with  $\text{NH}_3$  to form a yellowish-brown colloidal solution. The absorbance of the colored solution was measured at 425 nm, using a glass cell with 1 cm optical path length. Ammonium standards were prepared from ammonium sulfate (analytical grade, MERCK), after drying this salt at 100°C for about 1 h. New calibration curve was performed, when the Nessler's solution was replaced with freshly prepared one.

### FAES, FAAS and GFAAS Measurement Conditions and Operations

Operating conditions for FAAS, FAES and GFAAS, and the temperature programs for GFAAS are listed in Tables I–III. For GFAAS analyses we used pyrolytic tubes without platforms and matrix modifiers (wall atomization), absorbance signals were measured as peak heights. Three reference materials (NIST SRM-1646-Estuarine sediment, NIST SRM-2704-Buffalo river sediment and NIST USGS-GSP-1) were analyzed to ensure that accurate measurements had been made. For the preparations of reference samples, 0.10 g of SRM was weighed, and put in the Teflon vessel of a

TABLE I FAAS and FAES conditions\*

<i>Element</i>	<i>Na</i>	<i>K</i>	<i>Ca</i>	<i>Mg</i>	<i>Fe</i>	<i>Zn</i>	<i>Al</i>
Lamp current, mA			15	15	30	18	15
$\lambda$ , nm	589.1	766.5	422.7	285.2	248.2	213.9	309.2
Rate of $\text{C}_2\text{H}_2/\text{Air}$ (mL/min)	3.7/9.5	3.0/8.5	3.9/9.0	3.0/9.0	2.9/9.8	2.8/10.4	7.2/7.7**
Spectral bandpass, nm	0.2	0.7	0.7	0.7	0.2	0.7	0.7

\*Pneumatic nebulizer was used; \*\*Acetylene/Nitrous oxide.

TABLE II GFAAS conditions

<i>Element</i>	<i>Cd</i>	<i>Pb</i>	<i>Ni</i>	<i>Cr</i>	<i>V</i>
$\lambda$ , nm	228.7	283.3	232.0	357.8	318.4
Spectral bandpass, nm	0.7	0.7	0.2	0.7	0.7
Sample volume, $\mu\text{L}$	30	20	20	20	40
Lamp current, mA	3	7	30	16	20

TABLE III Graphite furnace programs

<i>Element</i>	<i>Step no.</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>
Cd	Furnace temp., °C	90	130	700	1600	2000
	Ramp time, sec	5	10	10	0	2
	Hold time, sec	15	10	25	6	5
Cr	Furnace temp., °C	90	130	1600	2500	2650
	Ramp time, sec	5	10	15	0	2
	Hold time, sec	15	20	20	5	8
Ni	Furnace temp., °C	90	130	1400	2500	2650
	Ramp time, sec	5	10	10	0	2
	Hold time, sec	15	15	25	5	6
Pb	Furnace temp., °C	90	130	750	1800	2100
	Ramp time, sec	5	10	10	0	2
	Hold time, sec	15	15	25	5	8
V	Furnace temp., °C	90	130	1200	2650	2650
	Ramp time, sec	5	10	10	0	2
	Hold time, sec	15	15	25	7	10

TABLE IV Comparison of the concentrations found by FAES, FAAS, and GFAAS with the certified values in NIST-SRMs, SRM-GSP-1, SRM-2704 and SRM-1646: comparison with the certified values

<i>Element</i>	<i>Found</i>			<i>Certified</i>		
	<i>GSP-1</i>	<i>2704</i>	<i>1646</i>	<i>GSP-1</i>	<i>2704</i>	<i>1646</i>
Na**	2.04 ± 0.17	0.68 ± 0.10	1.95 ± 0.13	2.08	0.76	2
K**	4.54 ± 0.14	1.97 ± 0.10	1.79 ± 0.13	4.57	2	1.63
Ca**	1.56 ± 0.18	2.40 ± 0.12	0.73 ± 0.16	1.46	2.6	0.83
Mg**	0.61 ± 0.04	1.17 ± 0.15	1.05 ± 0.10	0.596	1.2	1.09
Al**	8.31 ± 0.21	6.44 ± 0.26	6.48 ± 0.22	8.2	6.11	6.25
Fe**	3.0 ± 0.10	3.9 ± 0.30	3.3 ± 0.10	3.01	4.11	3.35
Mn	308 ± 0.30	554 ± 0.13	373 ± 0.35	310	555	375
Zn	115 ± 6.0	464 ± 15	152 ± 10	103	438	138
Cr	12 ± 3.0	129 ± 2.0	80 ± 3.0	13	135	76
Ni	11 ± 3.0	38 ± 7.0	27 ± 6.0	9.8	44.1	32
V	51 ± 3.0	94 ± 6.0	95 ± 2.0	53	95	94
Cd	55 ± 4.0*	3.4 ± 0.8	0.34 ± 0.10	56	3.45	0.36
Pb		163 ± 0.30	30 ± 3.0		161	28.2

\*Unit is in ng/g (ppb); \*\*Units are in (m/m)%, the others are in µg/g; The number of replicates (N) were 35, and the uncertainties is represented by the standard deviation (SD) values.

PARR-model-4746 high pressure decomposition system and 4.5 mL subboiled nitric acid and 1.0 mL concentrated HF were added. Lids were closed, Teflon beakers were inserted into stainless steel jackets and heated at  $150 \pm 10^\circ\text{C}$  for 6 h. After cooling, lids were opened, solutions were evaporated and the HF was removed by repeated evaporations to near dryness and by repeated additions of 2 mL subboiled  $\text{HNO}_3$ . The final residue was dissolved with 1 (m/m)% subboiled nitric acid solution and diluted to 50 mL with the same dilute acid solution. A blank was also prepared with the SRM standards to correct the elemental contributions from the reagents used in digestion. Each day, before analysis of aerosol samples, standard addition curves were prepared by the use of SRM's. Concentration of the element being measured in the samples, on that particular day, was determined in the SRM samples, in order to verify the accuracy of the method. If concentrations found were within  $\pm 5\%$  of the

certified value a second standard addition curve was set up by applying 5–10 mL aliquots of approximately 10 aerosol sample solutions. The slope of this standard addition curve was used to calculate the concentrations of the analyte in the rest of the samples using their measured signals. The concentrations determined in SRM samples by applying FAAS, FAES and GFAAS throughout the study and the certified values are given in Table IV.

## RESULTS AND DISCUSSION

### Analytical Performance Data

Three types of blank samples, namely, field blanks, filter blanks and acid blanks were used in this study. Field blanks consisted of Whatman-41 filters loaded to the sampler at the station and removed after operating the sampler for only 15 s. Field blank filters were then handled and analyzed like sample filters. Filter blanks (laboratory filter blanks) were prepared by digesting and analyzing a clean filter from every batch purchased. Acid blank consisted of only the same amount of reagents used for one sample in the digestion process. All blanks were analyzed by AAS, but field blanks only by INAA. The average concentrations of field blanks are given in Tables V and VI, respectively.

Acid and filter blanks provided information on contributions of filters, acids, water and laboratory operations on analytical blanks and the field blanks. Field blanks, on the other hand, provided information on the contribution of all procedures both in the laboratory, and in the field on the analytical results. The field blank values of elements were subtracted from all samples, whereas filter and acid blank results were used to develop and improve procedures to minimize blank contributions in the laboratory.

The concentration levels of most of the species monitored in air pollution studies are too low to be detected reliably. Therefore, for such data sets, some of the values can be below detection limits of the analytical technique, one should first determine the

TABLE V The average concentrations and  $\pm$  standard deviations (*SD*) of species determined from the field blanks by INAA technique. The numbers in parentheses are the parallel field blanks

<i>Element</i>	<i>Conc. <math>\pm</math> SD</i> (ng/g-filter)	<i>Element</i>	<i>Conc. <math>\pm</math> SD</i> (ng/g-filter)
Na	13000 $\pm$ 2800(12)	Br	720 $\pm$ 39(8)
Mg	10000 $\pm$ 3700(8)	Mo	21 $\pm$ 6.6(11)
Al	2600 $\pm$ 340(13)	Cd	28 $\pm$ 5.2(4)
Ca	150000 $\pm$ 17000(4)	Sb	13 $\pm$ 7.2(10)
Cl	71000 $\pm$ 14000(14)	Ba	3700(1)
K	81000 $\pm$ 19000(3)	Cs	36 $\pm$ 16(3)
Sc	1.1 $\pm$ 0.4(3)	La	1.7 $\pm$ 0.8(10)
Ti	3900 $\pm$ 1300(3)	Ce	39 $\pm$ 7.1(3)
V	17 $\pm$ 6(5)	Nd	660 $\pm$ 100(13)
Cr	1200 $\pm$ 570(13)	Sm	0.3 $\pm$ 0.1(11)
Mn	64 $\pm$ 19(12)	Lu	0.5 $\pm$ 0.2(3)
Fe	16000 $\pm$ 7400(8)	Au*	120 $\pm$ 37(7)
Co	59 $\pm$ 13(10)	Th	9.6(1)
Zn	1700 $\pm$ 420(9)	U	3.2 $\pm$ 0.7(3)
As	2 $\pm$ 2(6)	Hg	2.9 $\pm$ 0.9(6)
Se	120 $\pm$ 3(3)		

\*pg/g-filter



TABLE VI Average concentrations and standard deviations (SD) of species determined from filed blanks using atomic absorption and atomic emission spectrometry and ion chromatography. Numbers in the parentheses are the parallel filter samples

<i>Element</i>	<i>Average ± SD</i> (ng/g-filter)	<i>Element</i>	<i>Average ± SD</i> (ng/g-filter)
Na	17200 ± 1160(15)	Ca	11100 ± 3710(15)
Mg	3710 ± 1100(15)	Zn	780 ± 520(13)
Al	34900 ± 15400(15)	Ni	132 ± 51(12)
K	1540 ± 970(15)	Cr	155 ± 24(11)
Fe	715 ± 600(4)	Pb	60 ± 57(2)
Cu	390 ± 100(15)	Cd	46 ± 37(5)
Cl <sup>-</sup> *	28800 ± 17500(15)	V	38 ± 24(12)
NO <sub>3</sub> <sup>-</sup> *	17700 ± 9500(15)	NH <sub>4</sub> <sup>+</sup> **	Not detected (15)
SO <sub>4</sub> <sup>-</sup> *	7870 ± 4760(15)		

\*Ion chromatography; \*\*VIS spectrometry.

detection limit of the analytical technique. The detection limits depend on the nature of the samples and the sensitivity of the technique used. In INAA technique [32], the detection limit is controlled by several factors, like intensity of the neutron flux, the background in the  $\gamma$ -ray spectrum, composition and geometry of the sample and experimental parameters. Therefore, the detection limit in INAA is unique to each sample and determined by both the element under consideration and the presence of other elements. If the concentration of an element is too high, it yields a very high background level (compton peak of that element overlaps with the peak of other elements of low concentrations) in the spectra, and results in poor signal-to-noise ratio. In this case, the detection limits are higher than the actual concentration value in that sample for other elements. Because of the reasons explained above, generally valid detection limits cannot be provided for INAA technique. The averages of several detection limit calculations for the analytes are given in Table VII. Because of the compton peak of elements in the spectrum the detection limit calculated for Au is greater than its average concentration. This type of results can be seen, when the concentration of an analyte is too low in the sample.

In AAS analysis, the detection limits were calculated from the concentration of the element, which gave a signal three times higher than the standard deviation of 10-replicate measurements for one of the laboratory filter blanks. The detection limits for the elements determined are given in Table X as  $\text{ng g}^{-1}$  filter blank. The detection limits for IC and VIS spectrophotometry were calculated in a similar way, as for AAS, and were listed in Table VIII. All the detection limits calculated with the above criteria, were much lower than the concentrations of the corresponding elements, found in the aerosol samples.

In order to test the sample homogeneity on the filter and the reproducibility of the results obtained from INAA technique, one fourth of the aerosol sample was divided into six parts, and each part was weighed and analyzed, as different samples. In addition, three of these six samples were enclosed in polyethylene vials in order to check the loss of mercury from the samples during irradiation (Table IX). According to Table IX, the results showed an insignificant loss of mercury during the irradiations of samples. This result was expected, because of the unique property of the MITR-II reactor, in which irradiations can be done at room temperature. Almost the same results were

TABLE VII Calculated detection limits for the elements observed by the INAA and average concentration and standard deviation (*SD*) of the elements determined from the samples

<i>Element</i>	<i>Detection limit</i> (ng/g-sample filter)*	<i>Average conc.</i> (ng/g-filter)	<i>Element</i>	<i>Detection limit</i> (ng/g-sample filter)*	<i>Average conc.</i> (ng/g-filter)
Na	15000	180000 ± 15000	Cd	35	84 ± 66
Mg	7900	96000 ± 99000	In	1.0	5.8 ± 4.0
Al	5500	150000 ± 170000	Sb	1.2	160 ± 140
Ca	110000	400000 ± 350000	Ba	1200	6300 ± 3600
Cl	16000	190000 ± 130000	Dy	1.6	36 ± 24
K	9400	160000 ± 80000	Cs	2.1	88 ± 78
Sc	0.31	30 ± 37	La	3.1	92 ± 120
Ti	730	15000 ± 11000	Ce	5.2	150 ± 190
V	20	1300 ± 1200	Nd	17	840 ± 600
Cr	730	2600 ± 2400	Sm	0.1	13 ± 19
Mn	84	4500 ± 3300	Eu	0.5	20 ± 24
Ga	520	2100 ± 1700	Tb	0.2	12 ± 14
Sr	52	11000 ± 48000	Yb	0.3	6.7 ± 6.5
Fe	1500	150000 ± 130000	Lu	0.08	1.5 ± 1.3
Co	3.1	140 ± 100	Hf	0.8	17 ± 15
Zn	220	8100 ± 8300	Ta	1.8	130 ± 130
As	4.2	690 ± 710	Au	0.8	0.45 ± 0.73
Se	2.1	290 ± 200	Th	0.3	40 ± 78
Br	210	3700 ± 1700	U	7.3	14 ± 9.4
Rb	5.2	1800 ± 2200	Hg	2.1	31 ± 27
Mo	21	340 ± 500			

\*Detection limits in ng/27 cm<sup>2</sup> were converted to ng/g-sample filter.

TABLE VIII Calculated detection limits for the elements and ions determined by FAAS, FAES, GFAAS and IC

<i>Elements</i>	<i>Detection limit</i> (ng/g-filter blank)	<i>Elements/ions</i>	<i>Detection limit</i> (ng/g-filter blank)
Al(FAAS)	16000	Cd (GFAAS)	320
Na(FAES)	37000	Cr (GFAAS)	140
K(FAES)	8500	Ni (GFAAS)	470
Ca(FAAS)	97000	V (GFAAS)	260
Mg(FAAS)	17000	Cl <sup>-</sup> (IC)	580
Fe(FAAS)	30000	NO <sub>3</sub> <sup>-</sup> (IC)	580
Pb(GFAAS)	7900	SO <sub>4</sub> <sup>2-</sup> (IC)	690
Zn(FAAS)	6300	NH <sub>4</sub> <sup>+</sup> (VIS)	580
Cu(FAAS)	4100		

obtained (within 10% relative standard deviation) from the parallel samples for most of the trace and major elements determined. There was no significant difference between the results for samples enclosed in vials and in polyethylene bags. The large standard deviations observed for trace elements in this experiment are due to very low concentrations of these elements in some samples. As follows from the above results, the samples were homogeneous on the filter paper and the sample composition could be determined precisely by using INAA technique.

### Statistical Treatment of Data

Statistical summary of elemental concentrations obtained from 354 daily aerosol samples is given in Table X, which includes arithmetic and geometric mean concentrations with

TABLE IX The concentrations of elements determined by INAA from 6-parallel samples

<i>Element</i>	<i>N</i>	<i>Average ± SD</i> ng/m <sup>3</sup>	<i>Element</i>	<i>N</i>	<i>Average ± SD</i> ng/m <sup>3</sup>
Na	6	100 ± 7.3	Br	6	8.1 ± 2.3
Mg	5	120 ± 33	Mo	5	0.2 ± 0.09
Al	6	350 ± 17	Cd	6	0.3 ± 0.09
Ca	1	730	In	4	0.01 ± 0.01
Cl	6	130 ± 53	Sb	6	0.8 ± 0.2
K	3	190 ± 120	Ba	2	5.1 ± 2.5
Sc	6	0.07 ± 0.01	Cs	4	0.05 ± 0.03
Ti	5	17 ± 11	La	6	0.24 ± 0.02
V	6	3.5 ± 1.1	Ce	4	0.1 ± 0.1
Cr	5	9.3 ± 7.9	Nd	6	2.1 ± 0.9
Mn	6	10 ± 1.0	Sm	6	0.03 ± 0.0
Fe	6	320 ± 58	Yb	5	0.01 ± 0.001
Co	5	0.16 ± 0.13	HF	2	0.02 ± 0.02
Zn	6	24 ± 12	Au	5	0.002 ± 0.003
As	6	2.8 ± 0.2	Th	4	0.02 ± 0.01
Se	6	0.6 ± 0.5	U	3	0.03 ± 0.01
Hg	6	0.02 ± 0.01			

*N*: The number of samples in which detectable amount of elements observed.

the corresponding standard deviations, number of samples, median and mode values. This data set is the averaged results of INAA, AAS, IC and VIS. The arithmetic standard deviations of the analyte concentrations listed in Table X are comparable to their mean concentrations. High standard deviations are not unusual in environmental data sets and do not necessarily due to incorrect use of sampling and analysis procedures. The observed large standard deviations are due to large variability of the atmospheric concentrations of the elements over short periods of time. This originates from the variations in the meteorological conditions, physical and chemical transformations, air mass transport patterns and the variations in emissions affecting the receptor site. Mean concentrations of anions change between  $4.9 \mu\text{g m}^{-3}$  ( $\text{SO}_4^{2-}$ ) and  $0.92 \mu\text{g m}^{-3}$  ( $\text{NO}_3^-$ ) for the whole data set. Mean concentrations of trace and major elements change between  $410 \text{ ng m}^{-3}$  (Ca) and  $0.014 \text{ ng m}^{-3}$  (In and Yb). Major elements in the aerosol samples have mean concentrations (as  $\text{ng m}^{-3}$ ) of 380 (Na), 150 (Mg), 320 (Al), 180 (K) and 280 (Fe) for the whole data matrix. Trace elements like Pb, Zn and Br have the highest mean concentrations in the data set, as shown in Table X, and are  $17.0$ ,  $16.0$  and  $7.2 \text{ ng m}^{-3}$ , respectively.

### Distribution of Elements and Ions in the Aerosols

In general, a data matrix is generally treated as normally distributed values, and described with arithmetic mean and standard deviation, in which it is assumed that there is a symmetric Gaussian distribution. However, in an environmental data set affected by different pollution sources, the element generally follow a log-normal distribution. The distribution type of aerosol composition over a long period of time is dependent on the fluctuations in the meteorological conditions and source strength variations. Frequency distributions of pollutants are useful to search for similarities and differences among the components, which may help to understand processes that influence ambient levels. For a symmetric Gaussian distribution, the values of arithmetic mean, median and mode are identical. If the parameters increase in the order

TABLE X Summary Statistics of Turkish Western Black Sea Basin aerosols: arithmetic and geometric means, standard deviation, median and mode

<i>Element</i> (ng/m <sup>3</sup> )	<i>Number of</i> <i>samples</i>	<i>Arithmetic</i> <i>mean (SD)</i>	<i>Geometric</i> <i>mean (SD)</i>	<i>Median</i>	<i>Mode</i>
Na	340	380(300)	300(2.0)	300	200
Mg	302	150(130)	110(2.2)	120	50
Al	354	320(380)	210(2.6)	230	200
Cl	354	310(330)	220(2.3)	230	200
K	354	180(180)	140(2.1)	140	140
Ca	279	410(450)	270(2.8)	290	200
Sc	229	0.071(0.11)	0.045(2.6)	0.047	0.030
Ti	152	32(38)	20(2.7)	22	20
V	354	2.7(2.3)	2.1(1.9)	2.0	1.8
Cr	354	1.3(1.1)	0.87(2.7)	0.98	0.90
Mn	230	11(7.6)	8.7(2.0)	9.3	9.0
Fe	354	280(300)	200(2.4)	230	200
Ni	354	1.6(1.4)	1.1(2.4)	1.1	1.0
Cu	354	170(350)	41(4.2)	27	100
Co	195	0.23(0.26)	0.13(3.3)	0.14	0.10
Zn	353	16(18)	10(2.8)	10	12
As	230	1.6(1.6)	1.2(2.2)	1.1	1.3
Se	193	0.46(0.49)	0.30(2.9)	0.33	0.20
Br	230	7.2(3.4)	6.4(1.6)	6.5	6.4
Mo	194	0.44(0.28)	0.35(2.1)	0.39	0.30
Cd	354	0.28(0.30)	0.21(2.0)	0.22	0.20
Sb	230	0.37(0.30)	0.30(1.8)	0.30	0.25
La	230	0.23(0.36)	0.15(2.3)	0.15	0.15
Ce	179	0.32(0.64)	0.17(3.1)	0.18	0.18
Sm	230	0.032(0.055)	0.020(2.5)	0.021	0.020
Au*	204	1.3(2.8)	0.43(4.1)	0.41	0.1
Hg	166	0.046(0.030)	0.037(2.1)	0.040	0.037
Pb	354	17(14)	12(2.5)	13	10
In	89	0.014(0.010)	0.012(1.8)	0.012	0.010
Cs	153	0.14(0.14)	0.090(3.1)	0.10	0.10
Nd	136	1.4(1.3)	0.84(3.2)	0.88	0.45
Yb	144	0.014(0.022)	0.010(2.6)	0.010	0.0090
Lu*	108	2.6(4.3)	1.3(3.4)	1.5	1.5
Th	163	0.074(0.13)	0.040(3.2)	0.047	0.10
PM**	183	49(34)	37(2.6)	45	69
NO <sub>3</sub> <sup>-</sup> **	354	0.92(0.51)	0.79(1.7)	0.81	1.00
SO <sub>4</sub> <sup>2-</sup> **	354	4.9(2.9)	4.2(1.8)	4.1	3.2
NH <sub>4</sub> <sup>+</sup> **	354	1.4(0.72)	1.2(1.7)	1.3	1.4

\*pg/m<sup>3</sup>; \*\*µg/m<sup>3</sup>; PM: Particulate Matter

of mode, median, and arithmetic mean, then the upper tail of the distribution extends toward larger values and called as positively skewed. If the order is reversed, the distribution is called as negatively skewed. As it is seen in Table X, the arithmetic mean, median and mode values for almost all the measured species increase in the order of mode, median, and arithmetic mean indicating that the distribution of all variables are positively skewed. In the present work, the Kolmogorov-Smirnov (K-S) statistics were used to test the goodness-of-fit of the data to log-normal distribution. The K-S test involves the entire distribution of the examined variable, but not just its central value, and compares the empirical cumulative distribution function to that of the hypothesized distribution. In the case of log-normal distribution, the maximum absolute distance between the data and the hypothesized distribution is calculated to test the conformance of the two cumulative distribution functions. While the emissions

from sources may be approximately constant, the successive mixing and dilution of pollutants, as they are transported from source to receptor, results in a log-normal frequency distribution for the ambient concentrations measured at the receptor [5]. The frequency histograms and associated distribution curves for a crustal (Al), marine (Na) and a pollution derived (As) element are given in Fig. 2. The K-S test showed that concentrations of almost all of the measured species show log-normal distributions as in Fig. 2, which means that the composition of the aerosols is influenced by multiple sources.

### Comparison of the INAA Data with FAES, FAAS, GFAAS and IC Results

As mentioned above, 230 samples were analyzed for trace and major elements by INAA and about 354 samples were analyzed for 13 elements by AAS. The samples analyzed with INAA were also measured for trace and major elements by GFAAS, FAAS, FAES and IC (for Cl) techniques. Common elements, which were measured by using the mentioned techniques are Na, K, Ca, Mg, Al, Cr, Cd, V, Fe, Cl and Zn. The results obtained from each sample for the same elements were blank corrected and illustrated as scatter plots of each technique (see Fig. 3). As can be seen, most of the elements determined by different techniques are in good agreement. These elements are Mn, Al, Cl, Zn, V, Fe and Na. The agreement between the results obtained for Mg, Cd and K are fairly good but there is a little agreement in the results of Ca and Cr, which can be measured more accurately using AAS techniques. Although, the INAA technique can give reliable results for these elements, as well as spectrochemical methods, there are some requirements that have to be supplied in the case of INAA, like enough cooling and counting times. In this work, we could not supply enough cooling times for the long lived isotopes, which require at least 20 days. The reason of this disagreement between the results of these two elements, may be, the inefficient cooling time required for chromium (half life is approximately 1 month) and excess cooling for calcium (half life is 4.7 days).

In this study, we used chromium results obtained by GFAAS, because we could detect chromium only in 70% of the samples with INAA and the results were not very accurate, when compared to control standard SRM 1571 (Orchard Leaves). The observation statistics for Mg, K and Ca were less than 80% in INAA results, therefore, for these elements, the missing values were computed from the FAAS and FAES results.

The chlorine concentrations found by INAA and IC are almost similar, as for other elements, which have very close average values for both techniques. The scatter plots of the elements are fairly different from unity slope and zero intercept, which may be caused from the uncertainties in the analyses procedures and possible inhomogenities in the filter samples. The outlying data points, seen on the scatter plots of Fe, Cd, Al, K, Na, Cl and Mn are the results corresponding to a dust storm affected the samples concerned. These high concentrations caused by the Saharan dust transport to our sampling site on 23 April 1997. This was realized after using air mass back trajectory calculations, which will be presented in detail in a subsequent article.

Consequently, most of the elements measured by the above techniques have very large correlation coefficient ( $R$ ) and low intercept values. According to the presented results, all the above techniques can be successfully applied for the analysis of aerosol samples. Neither INAA, nor AAS/AES are superior to each other in some cases, as for

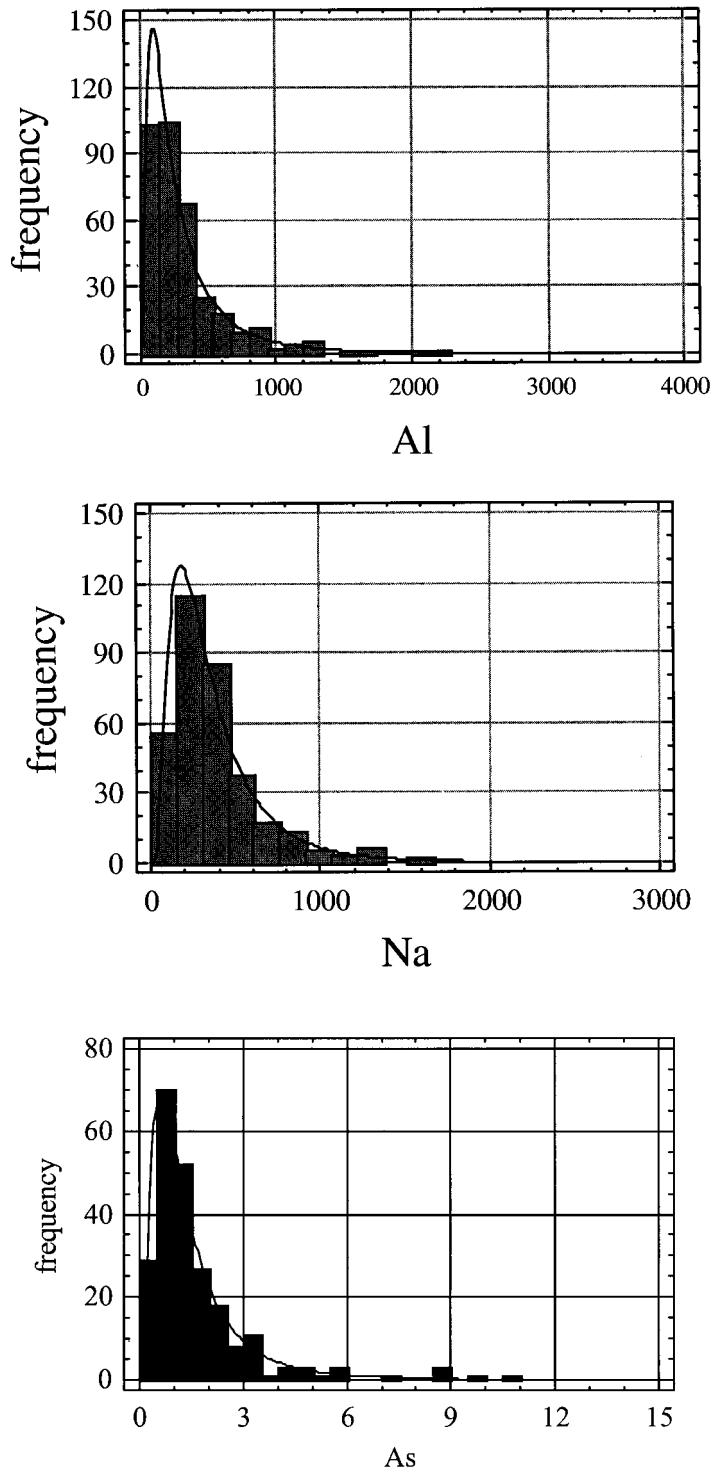


FIGURE 2 Frequency histograms and distribution curves of Al (crustal), Na (marine) and As (pollution derived element).

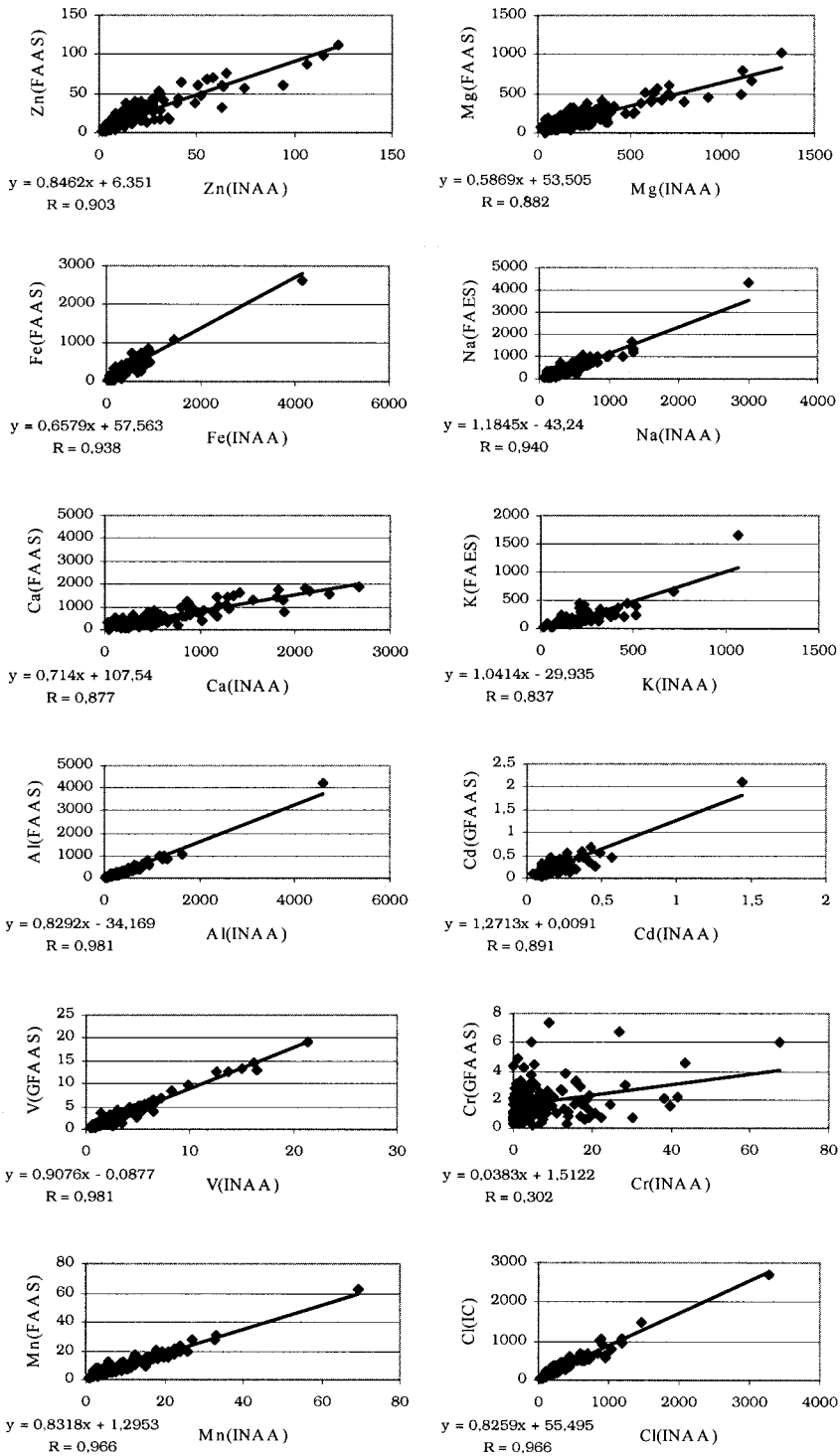


FIGURE 3 Scatter plots of elements determined by INAA, FAAS, FAES, GFAAS and IC methods.

example the application to environmental samples, rather than they are complementary techniques, and present good alternatives for environmental studies.

## CONCLUSIONS

Sample preparation, quality control procedures, and instrumental operating conditions for INAA, FAAS, FAES, GFAAS, IC and VIS spectrometry were presented. The detection limits calculated for all techniques were lower than the concentrations of the corresponding elements found in aerosol samples.

Homogeneity of the filter samples was determined by using INAA and it was found that six subsamples prepared from one of the aerosol sample were the same within 10% relative standard deviation (RSD) for most of the trace and major elements.

The most of the species determined in this study had high standard deviations which are usual behavior of atmospheric data sets due to physical, chemical transformations and meteorological conditions during transportation from emission sources to the receptor site. As a result of this high variability, almost all of the elements and ions showed log-normal distribution.

The elements like Mn, Al, Zn, V, Fe, Na, Mg, Cd and K determined by INAA and FAES, FAAS, GFAAS techniques gave fairly good results. In the same way, the Cl concentrations determined by both INAA and IC were in very good agreement with each other. There was no good agreement between the INAA results of Ca and Cr with the results obtained for these two elements from FAAS and GFAAS, respectively. Flame AAS for Ca and GFAAS for Cr gave more accurate results when compared to INAA results.

All the techniques used in this study are complementary to each other. In general, the elaborated analytical methods were successfully applied for the determination of a large number of trace and major elements, which were very useful in identifying pollution sources, source types and regions after combining this data with the upper atmospheric meteorological data. As will be presented in a subsequent article, we determined the crustal element compositions of regional aerosols by using this large data set and meteorological data in the form of air mass back-trajectories.

## Acknowledgment

The authors gratefully acknowledged BAYG of the Scientific and Technical Research Council of Turkey (TUBITAK) for supplying scholarships during INAA studies in USA.

## References

- [1] W. Baeyens and H. Dedeurwaerder, *Atoms. Environ.*, **25A**, 293–304 (1991).
- [2] N. Kubilay, S. Yemenicioğlu and A.C. Saydam, *Marine Pollution Bulletin*, **30**, 475–483 (1995).
- [3] G.H. Güllü, İ. Ölmez, S. Aygün and G. Tuncel, *J. Geophys. Res.*, **103**, 21943–21954 (1998).
- [4] N. Kubilay and A.C. Saydam, *Atmos. Environ.*, **29**, 2289–2300 (1995).
- [5] G. Hacısalıhoğlu, F. Eliyakut, İ. Ölmez, T.İ. Balkaş and G. Tuncel, *Atmos. Environ.*, **26A**, 3207–3218 (1992).
- [6] C. Migon and J.-L. Caccia, *Atmos. Environ.*, **24A**, 399–405 (1990).
- [7] L.E. Ranweiler and J.L. Moyers, *Environ. Sci. Technol.*, **8**, 152–156 (1974).



- [8] İ. Ölmez and N.K. Aras, *J. Radioanal. Chem.*, **37**, 671–677 (1977).
- [9] T.N. Mahadevan, B.S. Negi and V. Meenakshy, *Atmos. Environ.*, **23**, 869–874 (1989).
- [10] D.S. Lee, J.A. Garland and A.A. Fox, *Atmos. Environ.*, **28**, 2691–2713 (1994).
- [11] S. Okamoto, M. Hayashi, M. Nakajima, Y. Kainuma and K. Shiozawa, *Atmos. Environ.*, **24A**, 2089–2097 (1990).
- [12] S. Bauman, P.D. Houmere and J.W. Nelson, *Nucl. Instr. and Meth. in Phys. Res.*, **B22**, 322–324 (1987).
- [13] M.A.H. Eltayeb, R.E. Van Grieken, W. Maenhaut and H.J. Annegarn, *Atmos. Environ.*, **27A**, 669–678 (1993).
- [14] T.A. Cahill, *Nucl. Instr. and Meth. in Phys. Res.*, **B75**, 217–221 (1993).
- [15] G.M. Braga Marcazzan, P. Bonelli, E. Della Bella, A. Fumagalli, R. Ricci and U. Pellegrini, *Nucl. Instr. and Meth. in Phys. Res.*, **B75**, 312–316 (1993).
- [16] N.Z. Heidam, *Atmos. Environ.*, **28**, 1549–1555 (1994).
- [17] T. Berg, O. Royest and E. Steinnes, *Atmos. Environ.*, **27A**, 2435–2444 (1993).
- [18] M. Nimmo and G. Fones, *Anal. Chim. Acta.*, **291**, 321–328 (1994).
- [19] L.A. Debock, H. Vanmalderen and R.E. Vangriekin, *Environ. Sci. Technol.*, **28**, 1513–1520 (1994).
- [20] A.L.M. Loureiro, M.B.A. Vasconcellos and E.B. Pereira, *J. Radioanal. Nucl. Chem. Ser. A*, **159**, 21–28 (1992).
- [21] P. Krause, M. Kriews, W. Dannecker, C.D. Garbeschonberg and M. Kersten, *Fresen. J. Anal. Chem.*, **347**, 324–329 (1993).
- [22] K. Swami, C.D. Judd, J. Orsini, K.X. Yang and L. Husain, *Fresen. J. Anal. Chem.*, **369**, 63–70 (2001).
- [23] I. Szalóki, J. Osán, C.U. Ro and R.E. Van Grieken, *Spectrochim. Acta B*, **55**, 1017–1030 (2000).
- [24] I. Szalóki, J. Osán, A. Worobiec, J. de Hoog and R. Van Grieken, *X-Ray Spectrom.*, **30**, 143–155 (2001).
- [25] C.U. Ro, J. Osán, R. Van Grieken, *Anal. Chem.*, **71**, 1521–1528 (1999).
- [26] L.S. Hughes, J.O. Allen, P. Bhave, M.J. Kleeman, G.R. Cass, D.Y. Liu D.F. Fergenson, B.D. Morrical and K.A. Prather, *Environ. Sci. Technol.*, **34**, 3058–3068 (2000).
- [27] J. Osán, I. Szalóki, C.U. Ro, R.E. Van Grieken, *Mikrochim. Acta.*, **132**, 349–355 (2000).
- [28] L.S. Hughes, J.O. Allen, M.J. Kleeman, R.J. Johnson, G.R. Cass, D.S. Gross, E.E. Gard, M.E. Galli, B.D. Morrical, D.P. Fergenson, T. Dienes, C.A. Noble, P.J. Silva and K.A. Prather, *Environ. Sci. Technol.*, **33**, 3506–3515 (1999).
- [29] S.M. Talebi, *Int. J. Environ. An. Ch.*, **72**, 1–9 (1998).
- [30] T. Stahlschmidt, M. Schulz and W. Dannecker, *Spectrochim. Acta. B.*, **52**, 995–1001 (1997).
- [31] V.L. Foltescu, J. Isakson, E. Selin and M. Stikans, *Atmos. Environ.*, **28**, 2639–2649 (1994).
- [32] I. Olmez, *Instrumental Neutron Activation Analysis of Atmospheric Particulate Matter, in Methods of Air Sampling and Analysis*. (Lewis Publishers, Inc., 1989), 3rd Edn., Ann Arbor, 143p.