Asian Journal of Chemistry Vol. 19, No. 6 (2007), 4143-4150

Determination of Atmospheric Particulate Matter and Heavy Metals in Air of Tabriz City, Iran

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A network of seven sampling stations for the monitoring of elemental concentration of SPM in the air of Tabriz was established. Sampling was carried out from October 2002 and continued until September 2003. Instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS) methods were employed to obtain the monthly concentrations of V, Ca, Al, Fe, Mn, Sc and Zn in Tabriz air. The mean annual concentration (in $\mu g/m^3$) of 8 elements were found to be : Ca 12.065 (± 17.33 %), Al 2.207 (± 49.94 %), V 0.007 (± 21.47 %), Fe 1.829 (± 57.21 %), Sc 0.0007 (± 25.84 %), Mn 0.038 (± 36.07 %) and Zn 0.102 (± 25.17 %), Pb concentration has already been studied. The results of the study show that vehicle (traffic) pollution in Tabriz air is higher than WHO and EPA standards and natural and industrial pollution are exceeding international guidelines in some seasons.

Key Words: Suspended particulate matter, Tabriz city, Neutron activation, Heavy metals.

INTRODUCTION

For people who live in human ecosystems, either urban areas or agglomerations, good air quality is a very important requirement in any public health program. Moreover, more and more, data has proven the high impact of the atmospheric pollutants on health. Reports have shown the impact atmospheric pollutants can have on health when they are present in relatively high concentrations.

Atmospheric pollutants are responsible for both acute and chronic effects on human health[1,2]. The only major route by which particles enter the body through the respiratory tract. Relatively large particles are likely to get retained in the nasal cavity and in the pharynx. Very small particles are likely to reach the lungs and to be retained by them[3,4].

With due attention to interaction between water, soil and air, pollution of one of them, will lead to the pollution of another. Aggravation of air pollution causes pollution of water and soil. It means that risk of air pollution is 11 times more than water pollution and 16 times more than food pollution[5].

One part of SPM is metals. Airborne trace metals such as Pb, Cu, Mn, Zn, Fe, Ca, Mg, Cr, Ni and Cd are described as urban particulates. Heavy metals may come from many different sources in urbanized areas. One of the most important heavy metal sources is vehicle emission[6-8]. Atmospheric pollution is a major contributor to heavy metal contamination.

Tabriz is one of the most important industrial centers in the northwest of Iran. It has a population of some 1.227 million in an area of 2356 km^2 and is situated 1351 m above sea level. It is surrounded on the north, east and south parts by mountain ranges. There are some light and heavy industries on the northwestern, western and southwestern edges. There are also an oil refinery, a power plant and a petrochemical complex on the southwestern and a cement factory on the northwestern fringes of the city. On the other hand, the principal wind directions are from the east and the west.

Air pollution problem of the city of Tabriz is significant. In regard to air pollution, it is also among seven most highly contaminated metropolitan cities in Iran. Suspended paritculate matter (SPM) appears to have a particularly high rank on the list of pollutants. Pollution in this city is directly related to its increased population, heavy and light industries, increase of motor vehicles and cars with average age of 10 years and meteorological condition. Aside from the industrial SPM, city traffic has also been blamed as the major contributor to the air pollution[9]. Our studies focused on the determination of some of atmospheric heavy metals.

EXPERIMENTAL

Filtration has been the most common technique for sampling particulate matter. Samplers are set in seven site situated in polluted squares and in high traffic streets. Mean distance of these samplers from the center of a major road is 1-4 m at a height of 1.8-2 m. These samplers filtered *ca.* 1.2 m^3/h of air and were operating 24 h/day. The samples were collected weekly or monthly. Air sampling was started in October 2002 and continued until September 2003 (one year period). Glass fiber and Whatman filters were used for sampling, also methods of hot-plate digestion and ultrasonic extraction were used for digestion of filters. In hot-plate digestion procedure mixture of hydrochloric and nitric acid solutions are used.

In ultrasonic extraction method, each centrifuge tube containing a filter sample and nitric acid upright was placed in an ultrasonic bath (at room temperature). Ultrasonic energy (450 W ultrasonic power) was applied to the acid-immersed filter samples for a minimum of 0.5 h. All chemicals were of analytical regent grade and were provided by Merck (Darmstadt, Germany) and deionized water was used throughout.

Procedure of analytical methods

In laboratory, the collected filters were cut into four equal parts. First part was extracted by hot-plate digestion method. Second part was extracted by ultrasonic extraction (UE) method. The prepared solution by these two methods was analyzed by FAAS analytical technique. Two remained parts were used for activation analysis.

For quality assurance purpose, the FAAS method was further used to cross-check some of the INAA findings. Mn, V, Fe, Zn, Ca and Sc, were analyzed by the INAA method, while the other elements Cu, Al, Mn, Fe, V and Ca were analyzed by the FAAS method.

The measured absorbance of the unknown sample at the specific wavelength of each element was compared with the calibration curve generated from the prepared standard solutions of the same elements and from which the unknown elemental concentrations were determined. Atomic absorption measurement of Fe, V, Ca, Mn, Al and Cu were performed at the wavelength of 372, 318.5, 423, 279.5, 309.5 and 325 nm, respectively.

Third section of filters was used for short (SHL) and medium half life (MHL) elements and the fourth section was used for long half life (LHL) neutron activation analysis. The quarter section filter used for analysis of SHL and MHL elements were pressed into 13 mm diameter pellets and placed into a rabbit transfer system for neutron irradiation.

For LHL radionuclides; up to 30 pellets were placed into an aluminum can and received long neutron exposures inside the reactor core.

Sample transfer and handling systems for neutron activation analysis

Two rabbit transfer systems were designed for handling of the SHL and MHL radionuclides. The main system used the standard 5 cm diameter, 10 cm long plastic capsules containing the pellet and the stuffing material and carried it over a course of about 700 m to the neutron irradiation position in a period of about 28 s. After 0.25 MWh exposure to a flux of about 7×10^{11} cm^{-2} s^{-1} neutrons, it was automatically returned to the laboratory.

The capsule was manually opened in a shielded fixture and the bare pellet was dropped into a funnel where it was carried by means of a second pneumatic pellet transfer system (PTS) and positioned in front of a 60 cm^3 High Purity Germanium (HPGE) detector with a resolution of 2 keV at 1.33 MeV and 10 % relative efficiency.

The total transit and handling time after sample irradiation and before the start of the counting was about 2 min.

Each pellet, after the first count, was returned to a shielded and numbered cartridge position where it was stored for 1 h and then returned in front of the detector for subsequent counting for measurement of the MHL radionuclides.

Neutron activation analysis

Each irradiated palletized quarter section of each filter was transferred automatically to the detector position where it was counted for 5 min for SHL elements and subsequently was returned to a numbered cartridge storage position. There it was kept for 1 h for decay of the SHL radionuclides. Then the pellet was returned in front of the detector and counted again for another 0.5 h to obtain the spectrum of the MHL radionuclides. For LHL radionuclides, an aluminum can was filled with 30 pellets which were exposed to an integrated flux time of 8 MWh at the flux level of 5×10^{12} cm^{-2} s^{-1} neutrons in the core.

The irradiated aluminum can was removed from the core and was allowed to cool for 2 weeks. Each irradiated pellets was counted for 1 h and the spectrum of the LHL radionuclides was obtained.

MEASTRO software from ORTEC was used for taking the gamma spectra and the quantitative analysis was performed with the OMNIGAM software provided by ORTEC.

Standard reference materials from the International Atomic Energy Agency (IAEA) were obtained. In each case, different samples of the reference materials were prepared, irradiated and analyzed, from which concentration tables were made. Subsequent air filters were irradiated, counted, and analyzed in comparison with the said tables.

RESULTS AND DISCUSSION

Table-1 shows the average monthly elemental concentration of Zn, Ca, Sc, V, Al, Mn and Fe obtained from the seven sampling stations in Tabriz during 2002-2003.

TABLE-1
MONTHLY AVERAGE CONCENTRATIONS (μg/m^3) OF Mn, V, Fe, Zn, Sc, Ca, AND Al IN TABRIZ AIR BY AAS AND INAA METHODS

Month	Mn	V	Fe	Zn	Sc	Ca	Al
October 2002	0.038	0.008	1.354	0.116	0.0008	12.106	1.628
November 2002	0.027	0.006	2.126	0.128	0.0006	10.677	1.875
December 2002	0.023	0.007	0.983	0.133	0.0004	9.455	1.148
January 2003	0.018	0.005	0.908	0.142	0.0005	8.528	0.803
February 2003	0.025	0.005	0.756	0.121	0.0006	9.739	0.955
March 2003	0.036	0.007	0.850	0.107	0.0008	11.247	1.296
April 2003	0.057	0.009	0.992	0.094	0.0009	13.352	2.773
May 2003	0.055	0.011	1.987	0.075	0.0010	13.921	3.562
June 2003	0.059	0.008	2.539	0.086	0.0006	15.084	3.114
July 2003	0.044	0.008	3.680	0.073	0.0006	14.803	3.451
August 2003	0.039	0.008	3.323	0.068	0.0009	13.985	4.140
September 2003	0.035	0.010	2.848	0.082	0.0007	13.214	2.824

Fig. 1 shows the average monthly elemental concentration of Zn, V, Sc and Fe in Tabriz air during October 2002 until September 2003 (annual period).

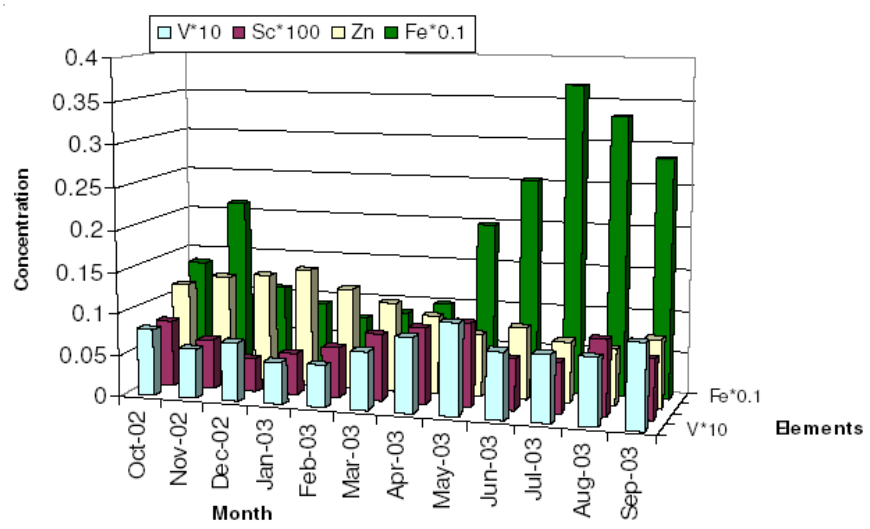

Fig. 1. Monthly average concentration of Zn, Sc, Fe and V (μg/m^3) obtained by INAA and FAAS

Fig. 2 compares the variation of the Mn concentration as obtained by two techniques of INAA and FAAS. This figure shows that, despite good agreement between these two techniques, AAS results for Mn produces higher standard deviations than INAA.

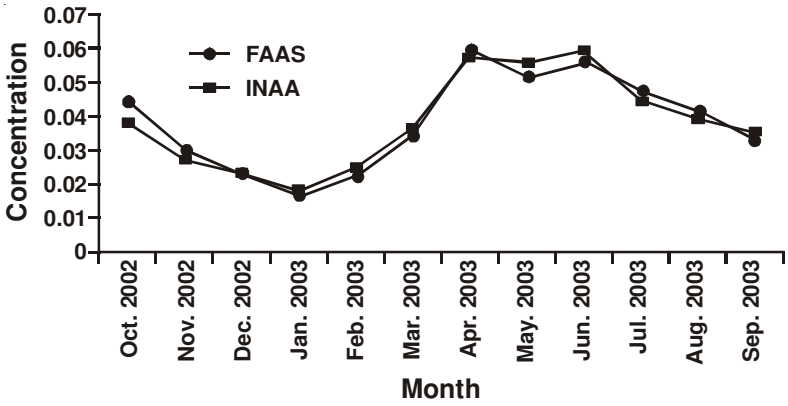

Fig. 2. Composition of the measured Mn concentration (μg/m^3) by the two technique of FAAS and INNA

Table-2 compares the seasonal variation of different elements in Tabriz air with those in Tehran and Shiraz.

TABLE-2
COMPOSITION OF THE SEASONAL AVERAGE CONCENTRATION (μg/m^3) OF DIFFERENT ELEMENTAL IN TABRIZ, TEHRAN AND SHIRAZ AIR

Elements	Tehran[10]		Shiraz[10]		Tabriz	
	Summer†	Winter‡	Summer	Winter	Summer	Winter
Fe	2.720	1.740	3.252	1.8910	2.5490	1.1090
Mn	0.098	0.058	0.065	0.0380	0.0480	0.0280
Pb	1.040	1.000	0.410	0.6690	0.4620	0.6480
Sc	0.002	0.001	0.001	0.0005	0.0008	0.0006
Zn	0.288	0.366	0.072	0.1000	0.0790	0.1250
Ca	7.610	6.310	15.305	11.2740	13.8650	10.2640
V	0.014	0.024	0.001	0.0070	0.0080	0.0060
Al	3.950	2.590	3.410	1.7510	3.3100	1.2840

†Spring and Summer; ‡Fall and Winter.

Table-3 tabulates the annual mean concentrations of 8 elements in Tabriz air and the corresponding WHO standards for some of these elements.

The average yearly Pb concentration in Tabriz was measured[9] as 0.555 μg/m^3 during Oct. 2002–Sep. 2003. This level is higher than the WHO guidelines of 0.5 μg/m^3 annual average (Table-3). This rather large Pb concentration seems to be due to heavy use of leaded gasoline by the motorists in Tabriz.

TABLE-3
ANNUAL MEAN CONCENTRATION (μg/m^3) WITH CORRESPONDING WHO GUIDELINES

Element	Annual mean	RSD (%)	WHO guidelines for urban areas
Pb	0.5550	33.78	0.5
Ca	12.0650	17.33	NA
Al	2.2070	49.94	NA
V	0.0070	21.47	0.05-0.2
Fe	1.8290	57.21	NA
Sc	0.0007	25.84	NA
Mn	0.0380	36.07	0.01-0.03
Zn	0.1020	25.17	NA

NA = Not applicable

Conclusion

The concentration of the traffic pollutant (Pb) in cold seasons (fall and winter) is more than hot seasons (spring and summer), which is due to the inversion phenomenon in cold months when the dispersion of pollutants dose not occur. Pb concentration is not affected by the wind direction due to the fact that Pb is mainly emitted by motor vehicles[9].

According to Table-2 the general levels of polluting elements in Tabriz, with the exception of Ca, were found to be lower than the Tehran. The main reason probably results from the presence of a cement factory located in the south west of Tabriz city.

Soil or construction industry related elements (Al, Ca and Fe) seem to have a high concentration pattern in spring and summer and a lower concentration in the fall and winter seasons.

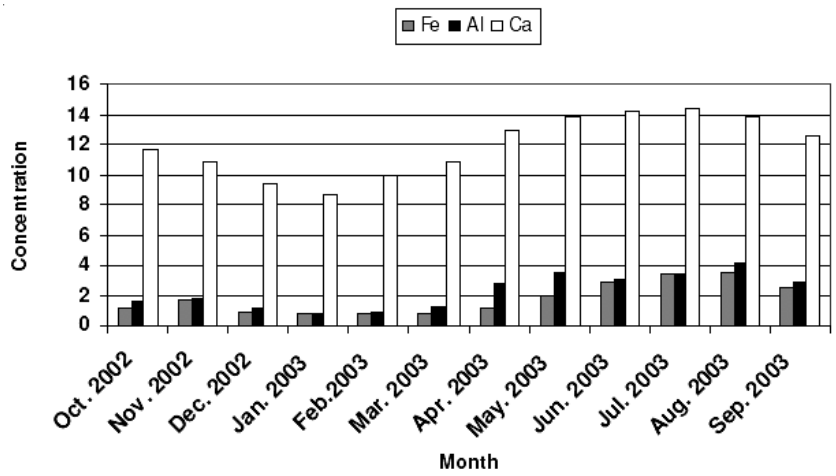

Fig. 3. Composition of the measured Fe, Al and Ca concentration (μg/m^3)

On the other hand, fossil fuel marker element (V) arises from both vehicular and industrial sources. Its higher concentration in the dry season could be related to roofing and road construction activities that use tar as the main material (Tables 1 and 2). Tabriz has a lower concentration of V than Tehran; it is rational to suggest that this is due to higher levels of traffic and a greater concentration of major industries in Tehran (Table-2). The WHO guidelines for vanadium in urban is 0.05-0.20 μg/m^3 and it appears that V pollution in Tabriz air is not considerable.

Concentration of Sc increased between April and May, while manganese annual average concentration in Tabriz air has been measured to be 0.038 μg/m^3, compared to the WHO recommendation for annual urban averages of 0.01-0.03 μg/m^3.

Summer high concentrations of soil related elements such as, Al, Ca and Fe are expected, because soil particles bearing these elements are produced by the resuspension of surface soil by the wind action which in turn depends on the moisture of the surface soil. Since the surface soil is wet and ice-covered in winter, generation of crustal particles is at minimum.

In general, trace metals concentrations follow the behavior of total suspended particulate matter (TSP) with higher concentrations during the day. Diurnal differences are more important for Pb and Mn, which present higher values in motor exhaust for Pb and for Mn indicating increased dust re-suspension during day hours. Thus, the atmosphere is cleaned up during the night when the traffic stops.

Comparing the results obtained from two filter extraction methods, *i.e.* hot-plate digestion and ultrasonic extraction, the latter is preferred because it is safer, precise and small amount of samples are lost.

With collected larger number of sample filters, much wider geographical distribution of the sampling stations and year long sampling period, it is expected that the elemental mean concentration amounts to be closer to the true mean values.

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(*Received*: 18 October 2005; *Accepted*: 28 March 2007) AJC-5534