

DETERMINATION OF SELECTED TRACE ELEMENTS IN AIRBORNE AEROSOL PARTICLES USING DIFFERENT SAMPLE PREPARATION*

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Determination of trace element concentrations in atmospheric aerosols is important because of their toxic effects on human health. Additionally, they are now widely used in source apportionment studies. There is a number of methods for sample preparation of ambient particulate matter. One of the most widely used is microwave-assisted digestion of filter-based samples. Since the water-soluble fraction is bioavailable, the aim of our study was to determine the concentration of selected trace elements (V, Cr, Mn, Ni, Cu, Zn, As, Cd, Sb, Tl, and Pb) in this fraction and compare it to the amounts obtained by two different microwave digestion procedures – one using a mixture of H₂O₂ and HNO₃ and the other using a mixture of HF, HCl, and HNO₃. The recoveries of the digestion procedures used were tested on certified reference material (NIST SRM 1648 Urban Particulate Matter). The procedures were applied to filters containing PM₁₀ particles collected at an urban background location in Ljubljana, Slovenia. Among the elements analysed, V, Zn, As, and Cd displayed the highest concentration within the water-soluble fraction, with Cr, Ni, Tl and Pb displaying the lowest concentrations. The comparison between the two applied digestion procedures showed that Cr, Ni, Sb and Tl were strongly bound to the sample matrix.

KEY WORDS: *chemical analysis, digestion, ICP-MS, metals, PM₁₀, urban aerosols, water-soluble fraction*

Atmospheric particles are generated through a variety of physical and chemical mechanisms, and are emitted into the atmosphere from numerous sources, by combustion, industrial and natural processes. They are involved in many atmospheric processes, and play an important role in reducing visibility, acid deposition, and the balance of radiation in the atmosphere, both directly and indirectly through cloud formation (1). There is a general agreement that airborne particulate matter is associated with adverse effects on human health (2). The concentration and composition of

particles may vary with size, time, and location, and depends strongly on the distance from the source, rate of emission, convective and turbulent diffusive transfer rates, on the efficiency of various removal mechanisms, and on meteorological parameters which affect vertical and horizontal distribution (3-5).

Toxicological studies have frequently implicated metal content (particularly water-soluble metal) as a possible harmful component of particulate matter. *In vivo* and *in vitro* studies have shown that metals generate reactive oxygen species, that activate cellular inflammatory response pathways (6). The potentially toxic elements are As, Cd, Cr, Hg, and Pb (7). Additionally, trace element content in particulate matter is often used in source apportionment studies.

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Metals are released into the atmosphere during combustion of fossil fuels and wood, as well as during high temperature industrial processes and waste incineration. Natural emissions result from a variety of processes acting on crustal minerals, including volcanism, erosion, surface winds, forest fires and ocean evaporation (8).

There are many different methods for sample preparation and chemical analysis of atmospheric particles. Among the non-destructive methods the most widely used are particle-induced X-ray emissions (PIXE), instrumental neutron activation analysis (INAA), and X-ray fluorescence spectrometry (XRF). Since recently, trace metals have also been analysed using inductively coupled plasma / mass spectrometry equipped with laser ablation introduction system (LA/ICP-MS) (9). Destructive analytical procedures include microwave-assisted digestion of filter-based samples, which is the most common method, followed by inductively coupled plasma / mass spectrometry (ICP-MS) or other spectrometric methods such as atomic absorption spectrometry (AAS). The choice of digestion reagents is for determination and characterization of multiple elements in ambient aerosols. Combustion and industrial processes are the primary source of carbonaceous and metallic particles, with soil erosion providing the major source of crustal material. The most abundant secondary constituents are sulphates, nitrates, and different organic compounds. Concentrated HNO_3 is usually the first choice because of its strong oxidising potential. However, it can not digest silicon-containing compounds and release elements bound to this siliceous matrix. For such components, HF is usually added (10, 11).

The water-soluble fraction is bioavailable and therefore represents a potentially harmful portion of atmospheric particles. The aim of our study was to compare the concentrations of selected trace elements V, Cr, Mn, Ni, Cu, Zn, As, Cd, Sb, Tl, and Pb in the water-soluble fraction obtained using two different microwave digestion procedures, one with a mixture of H_2O_2 and HNO_3 and the other of HF, HCl, and HNO_3 . The recoveries of the selected digestion procedures were tested on a certified reference material (NIST SRM 1648 Particulate Matter). The extraction procedures were applied to filters containing PM_{10} particles collected at an urban background location in Ljubljana.

METHODS

Sampling of PM_{10} was performed at an urban background location, Ljubljana-Bežigrad, Slovenia with a reference low volume sampler (Leckel, LVS3) over 24 hours in March and April 2006. Pre-fired quartz filters (Whatman) were used as a sampling substrate. Before the filters were weighed they were conditioned for 48 hours at 20 ± 1 °C and 50 ± 5 % relative humidity.

Filters with deposits were cut into three sub-samples using a punch made of quartz glass. To determine the water-soluble fraction, samples were sonicated in Milli-Q water at room temperature for 30 min. After extraction, the solution was filtered (Sartorius Minisart, pore size $0.2 \mu\text{m}$) and acidified with HNO_3 . All digestions were performed in a microwave oven (Milestone mLs 1200 mega). In the first procedure, a mixture of HNO_3 and H_2O_2 was applied. The sub sample was placed into a Teflon digestion vessel, and 3 mL of concentrated HNO_3 , 0.5 mL of 30 % H_2O_2 and 1 mL of Milli-Q water were added. In the second digestion procedure, a mixture of HF, HCl, and HNO_3 was used. Four millilitres of concentrated HNO_3 , 1 mL of concentrated HCl, and 1 mL of HF were added to the third sub-sample. Before addition, concentrated HF was diluted with Milli-Q water in the ratio 1:4. Digestion was accomplished in two phases. After the first phase, vessels were cooled, and 0.5 mL of H_3BO_3 (40 g L^{-1}) was added in order to complex excessive HF. Then the second phase was executed. Conditions for both digestions are described in Tables 1 and 2. After both procedures, samples were diluted with Milli-Q water to 50 mL, filtered through pre-washed filters (20 mL of 6 % HNO_3) and the first 20 mL of filtered sample was withdrawn.

The concentrations of the selected trace metals - V, Cr, Mn, Ni, Cu, Zn, As, Cd, Sb, Tl and Pb were determined by ICP-MS (Agilent 7500ce). Helium was used as the reaction gas in the collision cell, to reduce polyatomic interferences. For measurements, the following m/z were selected: ^{51}V , ^{53}Cr , ^{55}Mn , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{75}As , ^{111}Cd , ^{121}Sb , ^{205}Tl , ^{206}Pb , ^{207}Pb , and ^{208}Pb . For Pb, an average of three mass measurements is given. Elements Y, Sc, Ge, and Gd were used as internal standards during the measurement, and before the analysis the signal was optimised using Li, Y, Ce, and Ti.

Table 1 Digestion programme using a mixture of HNO_3 and H_2O_2

	Time / min	Power / W
Step 1	2	250
Step 2	2	0
Step 3	5	250
Step 4	4	400
Step 5	3	600

Table 2 Digestion programme using a mixture of HF, HCl, and HNO_3

	Time / min	Power / W
Phase 1		
Step 1	8	250
Step 2	5	400
Step 3	6	650
Phase 2		
Step 1	3	300

RESULTS AND DISCUSSION

Recoveries of certified reference material

The efficiency of both digestion procedures was tested using the certified reference material, NIST SRM 1648, Urban Particulate Matter. Their results for each element are shown in Table 3. The required recoveries for Pb and Cd in SIST EN ISO 14902 (Ambient Air Quality – Standard method for the measurement of Pb, Cd, As, and Ni in the PM_{10} fraction of suspended particulate matter) are range between 90 % and 110 %, while for As and Ni between 85 % and 115 %. Recoveries of all four metals by both procedures were in the required ranges. In addition (100±15) % recoveries were also achieved for Mn, Cu, and Zn. Lower recoveries were observed for V, Sb, and especially Cr (24 %) when using the $\text{HNO}_3/\text{H}_2\text{O}_2$ mixture. The HF/HCl/ HNO_3 mixture yielded more complete digestions, particularly for Cr (81 %) and Sb (increase from the 55 % recovery with the first digestion method to 81 %).

Problems regarding Cr characterisation in NIST SRM 1648 are documented in literature. It has been hypothesised that high soot content involves the presence of organic material that inhibits dissolution of Cr (11). Our results showed that HF not only decomposes silicates, but also enhances the dissolution of Cr from the organic matrix. The reference material used did not have a certified concentration for Tl. However, Tl concentration

determined after decomposition by the mixture of HF, HCl, and HNO_3 was significantly higher (3.5 times) than that yielded with the mixture of HNO_3 and H_2O_2 . This difference could probably be attributed to the binding of Tl to the silica matrix, which is decomposed in the presence of HF.

Concentrations of selected trace elements in ambient particulate matter

As filters were divided into sub-samples, the homogeneity of the filters was analysed first. All three sub-samples of one filter were digested in a mixture of HNO_3 and H_2O_2 . Relative standard deviations for most of selected elements were lower than 5 %, with the exception of Ni, Tl, and Pb. Higher deviations with Ni and Tl can be attributed to their concentrations which were very low, bordering the limit of quantification. The 10 % relative standard deviation for Pb could be due to non-homogeneity of the filter and/or the deposit.

Figures 1 and 2 show the results from the analysis of selected trace elements in ambient particulate

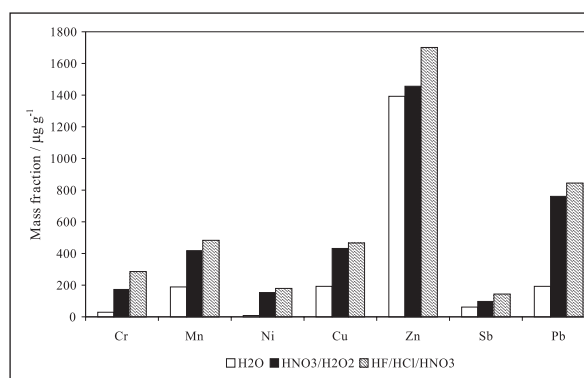


Figure 1 Average mass fractions of Cr, Mn, Ni, Cu, Zn, Sb, and Pb in PM_{10} collected in Ljubljana in the spring of 2005 after different sample preparations – dissolution in water, digestion with $\text{HNO}_3/\text{H}_2\text{O}_2$ and digestion with HF/HCl/ HNO_3

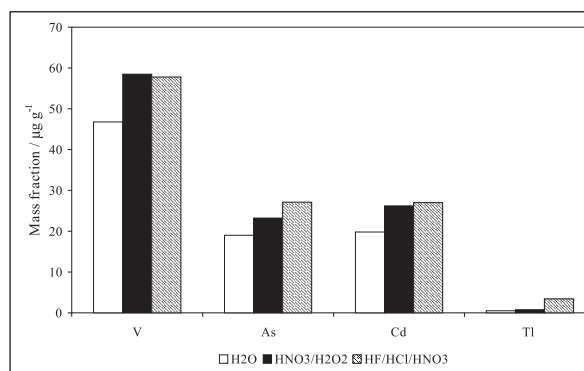


Figure 2 Average mass fractions of V, As, Cd, and Tl in PM_{10} collected in Ljubljana in the spring of 2005 after different sample preparations – dissolution in water, digestion with $\text{HNO}_3/\text{H}_2\text{O}_2$ and digestion with HF/HCl/ HNO_3

matter collected in Ljubljana-Bežigrad in the spring of 2006. They show the water-soluble fraction and the fractions after the decomposition by $\text{HNO}_3/\text{H}_2\text{O}_2$ and by $\text{HF}/\text{HCl}/\text{HNO}_3$ for these elements. The concentrations obtained after decomposition in the presence of HF can be taken as an approximation for the total concentration. Among the elements analysed, the most water-soluble were Zn, As, V, and Cd. For Zn and V the water-soluble fraction is about 80 %, while for As and Cd it is about 70 % of the total concentration. Mn, Cu, and Sb were moderately soluble in water, with the water-soluble fraction of about 40 % of the total concentration. Cr, Ni, Tl, and Pb were almost insoluble in water. Due to significant differences between acid decomposition with and without HF, it can be concluded that Cr, Sb, and Tl bind strongly to the matrix of atmospheric particles. However, a comparison with certified material shows a significant difference for Cr. The measured concentration in the reference material in the presence of HF was more than three times higher, while in the urban background aerosol the difference was only 1.7 times. The reason for this could be higher concentration of carbonaceous material in the reference material and also a different matrix of chromium compounds (e.g. silicates). A comparison with a study performed in Edinburgh (6) shows that the ratios of the water-soluble fraction and total concentration for the elements analyzed are very close. In Edinburgh too the most water-soluble elements were V, Zn, As, and Cd, with Mn, Cu and Pb being moderately soluble, and Cr and Ni almost insoluble.

Figure 3 shows water-soluble and total concentrations (after decomposition by the mixture of HF, HCl, and HNO_3) of selected trace elements in PM_{10} collected in Ljubljana-Bežigrad. Zn displayed the highest concentration within the water-soluble fraction (almost 30 ng m^{-3}), with the concentrations of Cu, Mn and Pb in the same fraction in the order of 4 ng m^{-3} . Concentrations of other elements were below 1 ng m^{-3} . A similar behaviour was also observed with total concentrations. The highest total concentration was that of Zn, and was in the range of the water-soluble fraction. The total concentration of Pb was about 15 ng m^{-3} (four times higher than in the water-soluble fraction), while concentrations of Mn and Cu were in the range of 10 ng m^{-3} . A significant total concentration was also observed for Cr (about 6 ng m^{-3}), and to a lesser extent for Ni and Sb (about 3 ng m^{-3}). In comparison with other studies performed in Europe (6, 12, 13), the total concentrations of V,

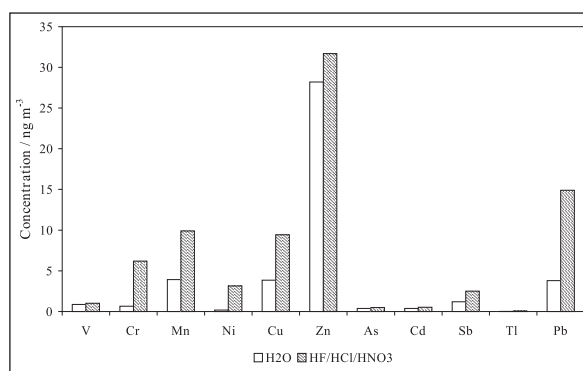


Figure 3 Water-soluble and total (after decomposition performed by mixture of HF, HCl and HNO_3) concentrations of selected trace elements in PM_{10} collected in Ljubljana-Bežigrad

Table 3 Results of both digestion methods for certified reference material (NIST SRM 1648, Urban Particulate Matter). 1) Digestion with a mixture of HNO_3 and H_2O_2 ; 2) Digestion with a mixture of HF, HCl, and HNO_3

Element	Certified value / $\mu\text{g g}^{-1}$	Measured value 1 / $\mu\text{g g}^{-1}$	Recovery 1 / %	Measured value 2 / $\mu\text{g g}^{-1}$	Recovery 2 / %
V	127±7	106	83	111	87
Cr	403±12	98	24	320	81
Mn	786±17	743	93	770	97
Ni	82±3	72	88	75	91
Cu	609±27	569	93	540	88
Zn	4760±140	4567	96	4370	92
As	115±10	123	107	109	95
Cd	75±7	76	102	67	90
Sb	45	25	55	36	81
Tl	/	2	/	7	/
Pb	6550±80	6269	96	6270	96

Ni, As, Cd, and Pb in Ljubljana are comparable to the concentrations measured at urban locations in Edinburgh and Vienna. Concentrations of Cu and Zn are about two times higher in Ljubljana. However, the most pronounced differences were observed for Cr and Mn, with concentrations four times higher in Ljubljana. This could not only be due to possible differences between the particle composition between the different regions, but also due to the sample preparation method used. In both studies the decomposition of the sample deposits was not done in the presence of HF (Vienna study: only extraction with concentrated HNO₃, Edinburgh study: hot extraction by a mixture of HCl and HNO₃) and therefore Cr and Mn bound to the silicate matrix were not released into the solution. The studies performed in Milan, Italy and Łódź, Poland (12) showed that concentrations of practically all analysed elements in these two cities were about an order of magnitude higher than in Ljubljana, Edinburgh, and Vienna.

CONCLUSION

Since the water-soluble fraction is bioavailable and therefore a potentially harmful portion of atmospheric particles, our study focused on the determination of this fraction of selected trace elements and on comparison of two different microwave digestion procedures used to determine them: one using a mixture of H₂O₂ and HNO₃ and the other a mixture of HF, HCl, and HNO₃.

Analysis of a certified reference material showed that both digestion procedures met the requirements of the SIST EN ISO 14902 for Pb, As, Cd and Ni. Recoveries of 100±15 % were also achieved for Mn, Cu and Zn. Very low recoveries of Cr, Sb, and V were obtained with the HNO₃/H₂O₂ mixture, while the HF/HCl/HNO₃ mixture yielded generally better recoveries particularly for Cr and Sb.

Zn, Cu, Mn, and Pb in the PM₁₀ samples collected in Ljubljana showed the highest concentrations in the water-soluble fraction, while Tl, Ni, As, and Cd showed the lowest. A comparison between the two applied digestion procedures has shown that Cr, Ni, Sb, Pb, and Tl bind strongly to the sample matrix. Total concentrations of the analysed elements were similar to concentrations obtained in Edinburgh and Vienna, while concentrations of most elements measured in Milan and Łódź were higher by about one order of magnitude.

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Izvleček**DOLOČEVANJE NEKATERIH ELEMENTOV V SLEDIVIH V ATMOSFERSKIH DELCIH**

Določevanje elementov v sledovih v atmosferskih delcih je pomembno zaradi njihovega toksičnega vpliva na človekovo zdravje. V zadnjem času se koncentracije teh elementov tudi zelo pogosto uporabljajo v študijah povezanih s porazdelitvijo po virih. Za določevanje elementov v sledovih se uporabljajo različne priprave vzorcev. Najpogostejši je razklop filtrov s pomočjo mikrovalovne peči. Ker je vodotopen delež tudi biološko dostopen, je bil namen naše študije določitev te frakcije posameznih elementov (V, Cr, Mn, Ni, Cu, Zn, As, Cd, Sb, Tl and Pb) in primerjava s koncentracijami po dveh različnih razklopih – prvi z mešanico H_2O_2 in HNO_3 ter drugi z mešanico HF, HCl in HNO_3 . Izkoristke uporabljenih razklopov smo preverili s standardnim referenčnim materialom (NIST SRM 1648 Urban Particulate Matter). Preverjena postopka smo uporabili na filtrih, ki so vsebovali delce PM_{10} , vzorčevane v Ljubljani, Slovenija. Med analiziranimi elementi so bili izrazito dobro topni v vodi V, Zn, As in Cd, najmanj pa Cr, Ni, Tl, in Pb. Primerjava med obema uporabljenima razklopoma je pokazala, da so Cr, Ni, Sb in Tl v delce izredno stabilno vezani.

KLJUČNE BESEDE: ICP-MS, kemijska analiza, kovine, PM_{10} , razklop, urbani aerosoli, vodotopni delež

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