Short Report

Optimization Method for Sequential Determination of Cu and Fe in Airborne Particulate Matter Collected on Glass Fiber Filters by Slurry Sampling FAAS

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Um método para determinação sequencial de Cu e Fe em material particulado atmosférico (APM) coletado em filtro de fibra de vidro por amostragem em suspensão e espectrometria de absorção atômica com chama é proposto. A otimização do método foi realizada utilizando-se uma massa de amostra seca em pó (filtro + APM) de 50 mg, dispersa em solução de ácido nítrico 0,5 mol L^{-1} e tratada por 10 min em banho ultrassônico. Os limites de detecção (n = 10) foram 4 e 14 µg g^{-1} para Cu e Fe no filtro, respectivamente. A repetitividade expressa como desvio padrão relativo foi melhor do que 7 e 8% (n = 3) para Cu e Fe, respectivamente. A exatidão do método foi confirmada analisando-se material de referência certificado de cinzas atmosféricas (BCR 176R). Os resultados obtidos para seis amostras de APM utilizando o método proposto não apresentaram diferenças significativas em comparação com os valores obtidos usando o método de extração ácida e determinação por espectrometria de massas com plasma indutivamente acoplado. O método analítico mostrou-se simples, rápido e confiável.

A slurry sampling flame atomic absorption spectrometric method for sequential determination of Cu and Fe in airborne particulate matter (APM) collected on glass fiber filters is proposed. The method optimization was carried out using a dry powdered sample (filter + APM) mass of 50 mg, dispersed in 0.5 mol L^{-1} nitric acid solution and under ultrasonic bath for 10 min. The limits of detection (n = 10) were 4 and 14 µg g^{-1} for Cu and Fe on the filter, respectively. The repeatability expressed as the relative standard deviation was better than 7 and 8% (n = 3) for Cu and Fe, respectively. The accuracy of the method was confirmed by analysis of the fly ash certified reference material (BCR 176R). The results obtained for six samples of APM using the proposed method showed no significant differences with those obtained after microwave-assisted acid extraction and determination by inductively coupled plasma mass spectrometry. The analytical method proved to be simple, fast and reliable.

Keywords: copper, iron, sequential determination, glass fiber filter, airborne particulate matter, slurry sampling, FAAS

Introduction

Metals in airborne particulate matter (APM) are originated from both natural (crustal, resuspension of soil, volcanic ash, etc.) and anthropogenic sources (smelters, fuel combustion, waste incineration and others).[1,2] Since the start of the industrial age, the human activities (such as mining, burning of fossil fuels, transport and construction) have resulted in additional release of metals to the environment.[3-5]

Among the various metals found in the chemical composition of APM, in urban areas, copper has been identified as a traffic-related element.[4] In contrast, iron is frequently present in APM due to the resuspension of soil dusts, and is therefore often considered to be an element derived from natural sources.[6] Epidemiological studies have shown that in urban areas, the continuous exposure to airborne particulate matter has the potential to affect the health of the population, causing various respiratory diseases (allergies, asthma and emphysema) and cardiopulmonary mortality. The chemical composition of this material is therefore of environmental and epidemiological interest.[1-7]

The determination of trace elements in APM collected on glass fiber filters is particularly difficult because of the refractory nature of the matrix. The total analyte concentration can only be determined after complete acid digestion in the presence of hydrofluoric acid, a procedure that is relatively time-consuming. The use of hydrofluoric acid is dangerous, but necessary for dissolving the silicates present in the filter and in APM. Several elements form volatile fluorides that could be lost during sample preparation.[1,3,8,9] Owing to these problems, instead of a total digestion, it is common in environmental analysis to use leaching with aqua regia, which does not allow the determination of the total content of an analyte in all situations. In addition, the resulting solution with a high concentration of dissolved solids can cause serious interferences in most of the atomic spectrometric techniques. This means that the solutions need to be highly diluted, which is often not possible in trace element determinations. Alternatively, the analyte has to be extracted, which is another time-consuming procedure, prone to analyte loss or sample contamination.[8-11]

The slurry sampling technique is an attractive alternative for pretreatment of samples prior to determination of metals and metalloids in atmospheric aerosols (APM and coal fly ash) by spectroanalytical techniques.[8,12-14] Carneiro *et al.*[15] determined Sb, Ni and V in APM collected on quartz filters using electrothermal atomic absorption spectrometry (ET AAS). Spiking recoveries close to 100% were obtained for Ni and Sb using an external calibration technique. For V, a calibration curve was constructed employing a blank filter. Ferreira *et al.*[16] and Macedo *et al.*[17] also used slurry sampling for the determination and speciation of Sb and As in APM by hydride generation atomic absorption spectrometry (HG AAS).

In recent years, several works have described the use of flame atomic absorption spectrometry (FAAS) as a multi-element technique for sequential determination of analytes in a variety of media.[16-19] The main advantage of the sequential determination lies in the automated optimization of the experimental conditions and consequently the shorter time required for the analysis. The sequential mode of the instrument allows the measurement of the absorbance at a sequence of wavelengths, using a scanning monochromator and a software for changing the operational conditions in short time intervals. This technique is of relatively low cost compared to sequential determination using inductively coupled plasma optical emission spectrometry (ICP OES).[18,20]

The aim of this study was to develop a fast, reliable and sensitive alternative to conventional methods for the determination of Cu and Fe in APM collected onto glass fiber filters, by combining the advantages of slurry sampling with those of fast sequential flame atomic absorption spectrometry (FS-FAAS), avoiding sample dissolution. To the best of our knowledge, this approach has not been used before for the analysis of APM.

Experimental

Instrumentation

A Varian model SpectrAA 240FS (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer with fast sequential module, equipped with a pneumatic nebulizer, having concentric tube with orifice diameter of 200 μm and nebulization spray chamber system was used for the analysis. A multi-element copper and iron hollow cathode lamp was operated under the conditions suggested by the manufacturer, applying a current of 10.0 mA. The most sensitive wavelengths for copper (324.8 nm) and iron (248.3 nm) were used, with bandwidths of 0.5 and 0.2 nm, respectively. The combustion mixture used was acetylene (flow rate of 2.0 L min^{-1}) and air (flow rate of 13.5 L min^{-1}), and the burner height was 13.5 mm (adjusted for copper). The nebulizer aspiration flow rate was kept in the range from 5.5 to 6.0 mL min^{-1}. An ultrasonic bath with power of 264 W and frequency of 40 kHz (Unique, Indaiatuba, SP, Brazil) was used for the preparation of the slurry. The acid extraction of Cu and Fe was carried out in a microwave oven (model ETHOS-plus, Milestone, Sorisole, Italy).

Reagents and solutions

Analytical grade reagents were employed throughout. A solution 65% m m^{-1} nitric acid (Merck, Germany) was used. Deionized water (resistivity of 18.2 MΩ cm) was obtained from a Milli-Q system (Millipore, Bedford, MA, USA). 50.0 mg L^{-1} solutions of Cu or Fe in 0.5 mol L^{-1} HNO$_3$ were prepared by diluting 1,000 mg L^{-1} stock metal solutions (Merck) in a 1% v v^{-1} nitric acid medium. Before use, all containers and glassware were soaked in 3.0 mol L^{-1} nitric acid for at least 24 h, rinsed three times with deionized water and dried in a dust-free environment.

Sampling and sample preparation

Six APM samples were collected on ash-free glass fiber filters (E55, 8 × 10 inch, Energética, Rio de Janeiro, RJ, Brazil) in Aracaju City (Sergipe State, Brazil), using a high-volume air sampler (Energética). The sampling flow rate used was 1,000 L min^{-1}, and the total sampling time was around 24 h (approximately from noon to noon of consecutive days). The sampled air volume was about 1,440 m^3. Each filter was placed in a clean polyethylene bag for transport and storage. The glass fiber filters were heated in a vacuum drying oven at 110-120 °C for 2 h prior to use. The filters were weighed (after moisture equilibration) before and after sampling to determine the net mass of the particulates collected. During the 24 h equilibration period, the filters were conditioned at a controlled temperature with variation lower than ± 3 °C, and constant relative humidity within a variation of ± 5%. After the final weighing, the exposed and blank filters were heated in a drying oven at 40-50 °C for 2 h, prior to being ground for 15 min in a ball mill of agate (Retsch, Düsseldorf, Germany) to a particle size lower than 63 μm. After grinding, the powdered samples were stored in polyethylene tubes. After the grinding of each sample, the ball mill was decontaminated by filling it with 20 mL of 5% v v^{-1} nitric acid solution, and leaving for 24 h. An unused filter was used to check the decontamination procedure. The certified reference material (CRM) BCR (Bureau of Reference, Brussels, Belgium) fly ash (BCR 176R) was used to check the accuracy of the procedure.

Slurry preparation

The sample slurry was prepared by mixing approximately 50 mg of dry powdered glass fiber filter containing the collected APM with about 15 mL of a 0.5 mol L^{-1} nitric acid solution in a 25 mL volumetric flask. The flask was immersed in an ultrasonic bath for 10 min. The final volume

was made up to 25 mL using 0.5 mol L^{-1} nitric acid solution. The slurry was pneumatically aspirated for the sequential determination of Cu and Fe by FS-FAAS. The blank was prepared in the same way as the sample, using a powdered unused filter, which contained Cu and Fe at concentrations lower than the limits of quantification.

Microwave-assisted acid extraction and determination by ICP-MS

The efficiency of the sample preparation procedure proposed in this work was checked by comparison of the results with data obtained using acid extraction in a microwave oven and analysis by inductively coupled plasma mass spectrometry (ICP-MS). An approximately 80 mg portion of the filter containing the collected APM was weighed directly into a polytetrafluoroethylene (PTFE) flask, to which was then added 4 mL of HNO$_3$, 1.5 mL of HCl and 3 mL of H$_2$O. The samples were subjected to microwave-assisted acid extraction using a model MLS 1200 MEGA digester (Milestone, Sorisole, Italy), with a program consisting of three steps: (step 1) hold time 5 min, temperature 25 to 85 °C; (step 2) hold time 15 min, temperature 85 to 210 °C; (step 3) hold time 25 min, temperature 210 °C.

After the extraction process, the solution containing particles that had not been decomposed was filtered through a cellulose acetate filter (Millipore, USA). The clear filtered solution was diluted to 30 mL with ultrapure water. Further dilution (3:10, v v^{-1}) was necessary prior to the analysis. The concentration of ^{63}Cu and ^{57}Fe was determined by ICP-MS (Perkin-Elmer SCIEX, model ELAN 6000, Thornhill, Canada). Argon gas with a minimum purity of 99.996% was obtained from White Martins (São Paulo, SP, Brazil). The sample introduction system equipped with a cross flow nebulizer and a Scott spray chamber was used. The parameters of nebulizer gas flow rate and applied power were optimized to maximize the intensities of M$^+$ ions and minimize the formation of oxide (Ce, CeO) and double positive charge (Ba^{2+}). The used instrument conditions were: flow rate of 1.15 L min^{-1}, radiofrequency applied power of 1.2 kW, autolens mode on, peak hopping measurement mode, dwell time of 25 ms, 50 sweeps by reading, 1 reading by replicate and 3 replicates. Platinum sampler and skimmer cones and an alumina injector of 1.5 mm i.d. were used. All samples were analyzed in triplicate. Marrero *et al.*[21] observed a homogeneous pattern of deposition on the filter for almost all the elements studied, allowing the use of different portions of the same filter for the analyte quantification with adequate precision.

Results and Discussion

The optimization was performed using univariate methodology, involving the parameters: concentration of the nitric acid, sonication time and dry powdered sample mass. All experiments were performed using a final volume of 25 mL. Only major elements were determined (Cu and Fe), since the AAS technique, used in this work, is of relatively low sensitivity. Certainly, the optimized method could be applied to other analytes.

Optimization of slurry preparation

Nitric acid concentrations from 0.0 to 1.0 mol L^{-1} for the slurry preparation were evaluated in order to establish the best medium that would improve the extraction of the analytes. The results showed that maximum sensitivity was achieved at a concentration of 0.25 mol L^{-1} and remained constant up to 1.0 mol L^{-1} for both metals. Variation in the nitric acid concentration did not cause significant changes in the intensity of the Cu signal. For Fe, a slightly better signal intensity was obtained at a nitric acid concentration of 0.25 mol L^{-1}. Interestingly, an absorbance signal in the absence of nitric acid for both elements was observed, but it was lower when nitric acid was used. A nitric acid concentration of 0.5 mol L^{-1} was used for the slurry preparation in all further experiments.

The effect of sample amount was also studied. Slurries were prepared using approximately 25, 50, 75 and 100 mg of powdered glass fiber filters containing APM, with 0.5 mol L^{-1} nitric acid as diluent and a final volume of 25 mL. The integrated absorbance signal was linear in relation to the sample mass (R > 0.99). Slurry prepared with a small mass was not conducive to sample homogeneity, and may result in lower precision. The use of a high mass eliminated these problems, but increased the likelihood of blockage of the FAAS nebulizer system. The adopted mass of 50 mg was found to be adequate for the sequential measurements of the analytes.

The effect of sonication time on the preparation of the slurries was studied in the range from 0 to 20 min, in a 5 min interval. In this range, there was no influence of sonication time on the intensity of the signal obtained for Cu; however, for Fe an increase in absorbance of about 40% was obtained for sonication periods ≥ 5 min. For times exceeding 5 min, the absorbance values showed no significant differences (at a 95% confidence level). A more efficient extraction of Fe from APM was achieved using sonication, as found previously.[22] In the absence of sonication, the solid particles of the slurry tend to agglomerate, decreasing slurry stability and/or causing possible blockage of the nebulizer system. With sonication, a better dispersion of the particles is easily seen, which decreases the possibility of blockage, as reported in the literature.[13-17] A sonication time of 10 min was adopted.

Using the above mentioned conditions, the extraction efficiency was studied by comparing the results for the sample slurry with those obtained for the liquid phase without slurry, after centrifugation at 4,000 rpm. For Cu, a recovery of 101 ± 9% was observed for the liquid phase, while for Fe the recovery was 90 ± 7%. These results demonstrate that extraction into the liquid phase of the slurry was practically complete for Cu, but probably partial for Fe, under the conditions employed. Filtration of the slurry prior to the analyte measurements was not used since it could be another source of sample contamination or analyte loss, especially considering the high amount of silica in the ground sample. In addition, for the sequential determination of both elements, the complete recovery required analysis of the slurry, and not the liquid phase.

Calibration

The calibrations curves were tested. The curve for the external calibration technique was prepared by dilution of the metal standard solution in a 0.5 mol L^{-1} nitric acid aqueous medium. The calibration curves for matrix matching technique were prepared using analyte additions in the presence of 50 mg of the unused filter, with and without APM, in a 0.5 mol L^{-1} nitric acid aqueous medium. All correlation coefficients were above 0.99. The equations of the calibration curves are presented in Table 1.

The slopes obtained for Cu were similar using either analyte addition or external calibration. However, for Fe, the slopes of the analyte addition curves, in the presence of loaded or unloaded filter, were about 25% lower than the slope of the external calibration curve, evidencing a matrix effect for Fe determination in the presence of the filter. For the sequential determination of Cu and Fe in filters loaded with APM, external calibration curves prepared in the presence of an unused filter were adopted, as a compromise condition. However, the determination of Cu could also be performed using external calibration with aqueous standard solutions without the filter.

Figures of merit

The figures of merit for the sequential determination of Cu and Fe in filters loaded with APM by slurry sampling using FS-FAAS are summarized in Table 2. A slurry of an unused filter without deposited APM was used as a blank to

Table 1. Equations of the calibration curves

Analyte	Calibration	Equation	Correlation coefficient
Cu	external calibration	$A = 0.0994\ C_{cu} - 0.0005$	0.9999
	analyte addition with loaded filter	$A = 0.1037\ C_{cu} + 0.0034$	0.9998
	analyte addition with a unused filter	$A = 0.1029\ C_{cu} + 0.0003$	0.9997
Fe	external calibration	$A = 0.0640\ C_{Fe} - 0.0003$	1.0000
	analyte addition with loaded filter	$A = 0.0477\ C_{Fe} + 0.1017$	0.9935
	analyte addition with a unused filter	$A = 0.0482\ C_{Fe} + 0.0051$	0.9996

A: absorbance; C_i: concentration of analyte i in mg L^{-1}.

Table 2. Figures of merit for the determination of Cu and Fe in APM collected on the glass fiber filter as slurry by FS-FAAS

Parameter	Cu		Fe	
	On filter / (μg g^{-1})	In air / (ng m^{-3})[a]	On filter / (μg g^{-1})	In air / (ng m^{-3})[a]
LOD / (3σ)	4	8	14	25
LOQ / (10σ)	15	27	45	80

[a]Values were calculated for Cu and Fe on the filter, based on a sample mass of 50 mg and also based on an air volume of 1,454 m^3.

determine the limits of detection (LOD) and quantification (LOQ).[23]

For both analytes, the absorbance values were close to zero, indicating concentrations below LOQ (10s, n = 10). The LOD and LOQ values for Cu and Fe on the filter material were calculated based on the use of 50 mg of filter, dilution to 25 mL with 0.5 mol L^{-1} nitric acid and a 24 h sampling interval (corresponding to an average sampled air volume of 1,454 m^3).

The CRM fly ash (BCR 176R) was used to confirm the accuracy achieved using either slurry sampling or the microwave-assisted acid extraction method. The results obtained for the concentrations of Cu and Fe in the CRM, with confidence intervals (at the 95% level, n = 3), are shown in Table 3. The values obtained for Cu were in agreement with certified values, with recoveries of 82.3 ± 7.6 and 92.2 ± 0.4% using slurry sampling FS-FAAS and microwave-assisted acid extraction followed by ICP-MS, respectively, demonstrating the good accuracy of both methods. The recovery for Fe was 112 ± 14%

using acid extraction in ICP-MS analysis. Unfortunately, it was not possible to determine the recovery for Fe using slurry sampling and FS-FAAS method due to the high Fe concentration in the sample, which made it impossible to weigh out a very small mass with adequate precision, while higher masses would cause an extrapolation of the maximum concentration of the linear part of the calibration curve.

Analytical application

Six samples of APM collected on glass fiber filters in Aracaju City were analyzed by the proposed method (slurry sampling FS-FAAS), and the results were compared to those obtained by ICP-MS after microwave-assisted acid extraction (Table 4). Statistical comparison using the paired *t*-test at the 95% confidence level, with five degrees of freedom, showed no significant differences between Cu and Fe values obtained by the two methods ($t_{calculated}$ for Cu = 2.13; $t_{calculated}$ for Fe = 0.80; n = 6; df = 5; $t_{tabulated}$ = 2.57).

The concentrations ± confidence interval (at the 95% level) of Cu and Fe found in the APM samples were between 17.3 ± 3.2 and 153 ± 7 μg g^{-1} for Cu, and between 410 ± 35 and 656 ± 29 μg g^{-1} for Fe. The precision expressed as the relative standard deviation (RSD) was better than 7 and 8% (n = 3) for Cu and Fe, respectively. These values reflect the good sample homogeneity obtained after grinding the filter containing APM. This work proposes an alternative method, according to which APM is ground together with the filter, resulting in a more homogeneous sample, as can be confirmed by comparing RSD obtained by

Table 3. Results obtained for the certified reference material fly ash BCR 176R (n = 3)

BCR 176R / (μg g^{-1})	Certified value / (μg g^{-1})	Slurry / FS-FAAS / (μg g^{-1})	Recovery / %	Acid extraction / ICP-MS / (μg g^{-1})	Recovery / %
Cu	1050 ± 70	968 ± 4	92.2 ± 0.4	865 ± 80	82.3 ± 7.6
Fe	13100 ± 500	n.d.	n.d.	14701 ± 1853	112 ± 14

n.d.: not determined; recovery = [(found value/certified value) 100] ± confidence interval at 95%.

Table 4. Results for Cu and Fe in AMP collected on glass fiber filter samples by slurry sampling FS-FAAS and by ICP-MS after acid extraction (mean values ± confidence intervals at 95%, n = 3)

Sample	Concentration in APM + filter							
	Cu				Fe			
	ICP-MS / (μg g^{-1})	RSD / %	FS-FAAS / (μg g^{-1})	RSD / %	ICP-MS / (μg g^{-1})	RSD / %	FS-FAAS / (μg g^{-1})	RSD / %
APM 01	102 ± 19	8	153 ± 7	2	311 ± 189	24	410 ± 38	4
APM 02	12.8 ± 1.4	4	17.5 ± 1.3	3	519 ± 174	14	540 ± 15	1
APM 03	16.7 ± 2.4	6	17.3 ± 3.2	7	697 ± 164	10	656 ± 31	2
APM 04	50.8 ± 3.7	3	57.2 ± 5.4	4	520 ± 153	12	496 ± 48	4
APM 05	78.3 ± 2.2	1	90.8 ± 2.7	1	564 ± 52	4	533 ± 5	0.4
APM 06	111 ± 9	3	133 ± 11	3	488 ± 45	4	595 ± 118	8

the proposed method with those obtained by acid extraction ICP-MS, as shown in Table 4.

The filters were loaded with masses of APM between 80.7 and 111.4 mg, corresponding to 53.3 and 84.6 μg APM m^{-3} of air. The average concentration of APM in the urban area of Aracaju City was 68.3 μg m^{-3} (n = 6). The results obtained by the proposed method were re-calculated to express the concentrations of the analytes in the air, considering a mean air volume of 1,454 m^3 sampled over 24 h. The concentrations obtained were between 32.4 ± 5.9 and 237 ± 11 ng m^{-3} for Cu, and between 470 ± 44 and 913 ± 44 ng m^{-3} for Fe. The average concentrations of Cu and Fe in air were 122 and 661 ng m^{-3}, respectively. The results, expressed as average concentration ± confidence interval (at the 95% level, n = 3) are summarized in Table 5. The United States Occupational Safety and Health Administration (OSHA) exposure limits in air are 1.0 mg m^{-3} for soluble Fe salts (as Fe) and for Cu dusts and mists (as Cu).[24,25] The concentrations measured in Aracaju City were below these maximum allowed limits.

Table 5. Results for determination of Cu and Fe in air from Aracaju City, Sergipe State, Brazil (mean value ± confidence interval at 95% (n = 3)

Sample	Concentration of APM / (μg m^{-3})	Element in air / (ng m^{-3})	
		Cu	Fe
APM 01	53.3	237 ± 11	470 ± 44
APM 02	76.0	32.4 ± 2.3	739 ± 21
APM 03	84.6	32.4 ± 5.9	913 ± 44
APM 04	59.5	89.4 ± 8.5	575 ± 56
APM 05	71.0	138 ± 4	602 ± 6
APM 06	65.4	203 ± 17	669 ± 132

The results can be compared with measurements in other urban areas. Levels of Cu and Fe in the Industrial District of Santa Cruz (Rio de Janeiro, Brazil) were higher than the average values found in Aracaju (Cu = 122 ng m^{-3} and Fe = 661 ng m^{-3}) due to the many industrial activities around

the sampling area. The average concentrations of Cu and Fe were 2.7 (335 ng m^{-3}) and 58.8 (38903 ng m^{-3}) times higher, respectively, than the values found for Aracaju.[26] In La Plata City (Buenos Aires, Argentina), the concentration of Cu was 4.1 (29.5 ng m^{-3}) times lower and of Fe was 1.8 (1183 ng m^{-3}) times higher.[27] In an open area called Porto de Aratu in Salvador City (Bahia, Brazil), a similar average value was found for Cu (121 ng m^{-3}), while the average concentration of Fe (328 ng m^{-3}) was twofold lower. Near an office building, the average concentrations of Cu and Fe in the air were 5.8 (21 ng m^{-3}) and 2.9 (226 ng m^{-3}) times lower, respectively, than found in the present work, demonstrating that the concentrations can vary depending on the activities around the sampling area.[28]

Conclusions

A slurry sampling method using FS-FAAS was developed for the sequential determination of Cu and Fe in powdered glass fiber filters containing samples of airborne particulate material. The proposed method is simple, fast and reliable, and is suitable for routine applications. The analytical features (precision, limits of detection and accuracy) indicate its efficiency. However, for Fe an unused filter should be used for external calibration to avoid non-spectral interferences. The calibration using powdered unused filter, required for Fe, is simpler and safer than the use of HF in a total digestion. Slurry sampling is environmentally friendly, and less subject to contamination or analyte loss, compared to conventional sample digestion. Average concentrations of Cu and Fe in airborne particulate matter collected in Aracaju City were below the maximum allowed limit values set by OSHA.

Acknowledgements

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