JAAS

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/jaas

Assessment of sample preparation methods for the analysis of trace elements in airborne particulate matter

D. Salcedo[1,*], J. P. Bernal[2], O. Pérez-Arvizu[2], E. Lounejeva[3]

[1]UMDI-J Facultad de Ciencias, Universidad Nacional Autónoma de México, Blvd. Juriquilla 3001, Querétaro, 76230, México
[2]Centro de Geociencias, Universidad Nacional Autónoma de México, Blvd. Juriquilla 3001, Querétaro, 76230, México
[3]Instituto de Geología, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, D.F. 04510, México (now at CODES, University of Tasmania, Private Bag 126 Hobart 7001, Australia)

ABSTRACT

The determination of trace element composition of airborne particles usually requires dissolution in acidic media followed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis. Analytical methods are usually validated on NIST SRM 1648 and 1648a, but without any further discussion regarding their application to real atmospheric samples. Here, we present an assessment of 5 digestion methods (over a hot plate and using a microwave system) for SRM 1648a and atmospheric particles based on the analysis of 30 elements by ICP-MS. Recoveries of NIST-certified elements for SRM 1648a confirm that a digestion method using HNO_3/HF on a hot-plate yields acceptable recoveries for most of the NIST-certified elements (with the exception of Cr). By conducting the elemental analysis in triplicated samples of particles collected on PTFE filters, we determined that the analytical method is reproducible within 9% for real PM samples. Heterogeneity of the reference material and atmospheric samples, as well as differences in chemical composition and particle size between both, suggests that uncertainties related to the dissolution of trace elements using acidic mixtures are not well characterized.

1. INTRODUCTION

The chemical characterization of airborne particles is an important step in understanding and addressing their effects on climate[1] and human health[2]. In particular, determination of trace elements in the particulate matter (PM) is an essential aspect to consider because it can be helpful in identifying particle sources and their contribution to the fine mass atmospheric concentration[3]; moreover, the presence and concentration of certain trace elements can be responsible for specific negative health effects[4,5].

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is usually the method of choice for the analysis of trace element concentrations in particulate matter because of its versatility and low detection limits. However, sample collection and preparation methods applied are quite variable, and frequently involve the collection of PM on filters, followed by acid digestion[6]. Collection of PM can be done using equipment with flows from 5 L to 1.13 m^3 per minute, either on PTFE or cellulose filters. Acidic solutions are also very diverse and usually contain HNO_3 mixed with HF, $HClO_4$, H_3BO_3, or HCl, and, occasionally H_2O_2. Additionally, digestions are done on hot-plates, or using microwave or ultrasound[7-15]. Each methodology have its own sources of errors and uncertainties (due to sample mass, possible contamination sources, and/or efficiency of digestion), which should be taken into account when comparing data and using it for atmospheric studies; nevertheless, they are usually not discussed.

Analytical methods for the determination of trace elements in PM are usually validated using the National Institute of Standards and Technology (NIST) Standard Reference Material Urban Particulate Matter (SRM 1648 and 1648a)[16], because it is assumed to have a similar matrix as the airborne aerosol. Analyte recoveries are generally calculated based on the analysis of the SRM and extrapolated to PM samples without further testing, even though the differences in size distribution and chemical composition might suggest the contrary. Although few studies perform reproducibility tests by analyzing duplicate PM samples collected on filters (i.e. samples collected side to side)[12], there is no discussion on the suitability of SRM 1648(a) (throughout the text, we will use this term to refer to both, 1648 and 1648a reference materials) as a reference material for PM, nor the efficiency of the digestion methods on real particles samples.

On the other hand, atmospheric chemical data obtained with almost any analytical technique (on- or off-line) usually have relatively large uncertainties, which become evident when comparing datasets from different instruments or sampling systems, even when collocated side by side[17,18]. In fact, precisions of 25% and accuracies of 40% are considered acceptable in atmospheric measurements[19]. Such measurements are equally useful for atmospheric studies, as has been proven by the constant advances in the understanding of atmospheric chemical processes based on *in situ* studies. However, the sources of poor comparisons or large errors generally remain to be further studied.

In this study we assess the best dissolution method for SRM 1648a using different acidic mixtures (containing HNO_3 mixed with HF, HCl, $HClO_4$, and/or H_2O_2) and two digestion methods (microwave and acid reflux). We also evaluate the efficiency and reproducibility of the digestion methods when applied to real samples (atmospheric PM collected on PTFE filters). In addition, we critically discuss the suitability of SRM 1648(a) as a reference material for the analysis of trace elements in airborne PM.

2. EXPERIMENTAL

2.1 Reagents and materials

Sample preparation was carried out in a class 100 class clean laboratory at Centro de Geociencias, UNAM, under laminar flow hoods except those experiments requiring the use of $HClO_4$, which were carried out in a similar facility equipped with specialized extraction hoods at Instituto de Geología, UNAM. All samples were dissolved in PTFE beakers (round interior Savillex vials 15 - 22 mL; or 45 mL vessels for the microwave system) using ultrapure deionized water (18.2 mΩ cm, Arium 611, Sartorius) and triple-distilled acids. After digestion, all samples were stored in high-density polyethylene (HDPE) containers. Blanks were always below detection limits, which are discussed in section 2.4.

2.2 Standards and samples

NIST SRM 1648a was stored in a dark flask inside a desiccator to reduce any residual moisture content. Aliquots of ~5 mg were weighted for digestion. The homogeneity of sample sizes of 5 mg or larger is established in the NIST Certificate of Analysis (CoA) of SRM 1648a[16]. The CoA also confirms the equivalence of SRM 1648a and its parent material SRM 1648, which is commonly used in previous reports in the literature.

Triplicate $PM_{2.5}$ samples were collected on PTFE filters (47 mm with polymethyl-pentene (PMP) support, Pall Corporation) using Minivol Portable Air Samplers (Airmetrics, Eugene Oregon, US) with an air flow of 5 L min^{-1} at the roof of Centro de Geociencias at UNAM campus Juriquilla in Queretaro (20° 42' 8.49" N, 100° 26' 49.24" O) from November 2010 to April 2011. The site is located on a 2-story building (15 m), at least ~500 m away from low traffic avenues and corresponds to a suburban environment. Three Minivols were placed next to each other for periods ranging from 5 to 7 days, during which 0.1 - 0.6 mg of PM were collected. A total of five triplicate samples were obtained. For the purposes of this study, each set of triplicates is assumed to be of identical chemical composition.

Prior to weighting and collection, filters were washed with deionized water and dried in a laminar flow hood; then, they were preconditioned for 24 hr in the same room where they were weighted.

The filters were always handled with clean PTFE-tipped tweezers and powder-free nitrile gloves. Clean polypropylene petri-dishes were used for storage until filters were loaded in the Minivols. After sample collection, the filters were returned to their corresponding petri-dish and transported to the clean laboratory for conditioning before weighting them. Prior to digestion, the PMP support was removed. Blank filters were also digested along the airborne PM samples.

2.3 Sample digestion and preparation

We assessed five digestion methods (described in Table 1) for SRM 1648a, using a hot-plate and pressurized microwave heating. For PM samples, only acid-reflux was assessed using three different acid mixtures (HNO_3/HF, HNO_3/HF/$HClO_4$, and HNO_3/HCl). The HNO_3/HF mixture was used because of its simplicity and prior reports of good recoveries[8,10]. Previous reports describe the addition of H_3BO_3 to complex fluoride ions and help dissolve insoluble fluorides formed during digestion with HF[10]; however, in order to avoid a complex mass spectra, potential sample contamination, and nebulization problems we instead removed HF by evaporation. Destruction of the pervasive organic material in SRM 1648a and airborne PM by the addition of $HClO_4$ or H_2O_2 was tested. We also tested the US EPA recommended method for the extraction of filter-collected PM for metal analysis by ICP-MS[7], which is based on a HNO_3/HCl (3:1) mixture. Finally, whilst microwave digestion is commonly used for the digestion of SMR1648(a) due to the reduced times needed for digestion, we were unable to fully assess its potential because of the large size of our vessels (45 mL), which made it impractical for our purposes, thus it was only tested for the dissolution of SRM 1648a using HNO_3/HF mixture.

Samples (SRM 1648a or PM collected on filters) were placed inside the PTFE vials together with the corresponding acid mixture, and the closed vials were left on a hot-plate (temperature-controlled $\pm 0.1^{o}$C) during different periods (Table 1). Because SRM 1648a consistently left a black residue, the mixture was centrifuged and the supernatant separated before the next step. In contrast, the solution resulting from the digestion of the filter samples was consistently clear and no residue was observed other than those on the filter, thus the centrifuge step was obviated. Microwave digestion was carried out on a Mars 5Xpress system (CEM Corporation) following a procedure based on Kulkarni *et al.*[10]: temperature was ramped in 10 minutes from ambient to 100^{o}C with a pressure setting of 100 psi, followed by a 15 minutes dwell; then, the temperature was ramped again in 10 minutes to 200^{o}C and 200 psi, with a final 15 minutes dwelling. After digestion the samples were evaporated to dryness to remove excess HF and, when required, ~100 µl of H_2O_2 were added during the evaporation step. Finally all samples were re-dissolved in 2% HNO_3 prior to analysis by ICP-MS. All SRM 1648a samples were diluted to 50 mL, and the PM samples to 10 mL. This allowed us to achieve concentrations below 100 ng/mL for most elements in the solution to be introduced in the ICP-MS. For the analysis of Mg, Al, Zn, Ti and Pb in SRM 1648a, an additional 1/50 dilution was required due to their higher concentration.

2.4 ICP-MS analysis

All the analyses were carried out using a Thermo X-Series II ICP-MS at Centro de Geociencias, UNAM, (instrumental parameters are listed on Table 2) using the Xs cones and unpressurized hexapole, with a cyclonic spray chamber and a microconcentric nebulizer with a 1000 µl/min sample consumption rate. The following isotopes were analyzed: ^{26}Mg, ^{27}Al, ^{47}Ti, ^{51}V, $^{52,53}Cr$, ^{55}Mn, ^{57}Fe, ^{58}Ni, ^{59}Co, ^{65}Cu, ^{66}Zn, ^{69}Ga, ^{75}As, ^{78}Se, ^{85}Rb, ^{88}Sr, ^{90}Zr, $^{95,98}Mo$, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{133}Cs, $^{135,137}Ba$, ^{139}La, ^{140}Ce, ^{146}Nd, ^{147}Sm, $^{206\text{-}208}Pb$, ^{232}Th, and ^{238}U. Oxide levels were monitored at the beginning of each analytical session by measuring the $^{140}Ce^{16}O/^{140}Ce$ proportion. The instrument was tuned to yield < 3% CeO^+.

Calibration curves were gravimetrically prepared from dilutions of Inorganic Ventures (Christiansburg, Virginia, US) 71A and 71B reference materials in the 0 - 100 ng/g range for the aforementioned isotopes.

Indium was used as internal standard (IS) for isotopes with m/z^+ < 115 uma, except for As and Se where Ge was used as IS; for the heavier isotopes In and Bi were used as IS. In order to assure the exact same concentration for the ISs in the samples and standards, both were diluted before ICP-MS analysis using 2% HNO_3 which was previously spiked with the ISs at 50 ng/g.

Detection limits (listed in Table 3) were calculated as the average signal of blanks plus three times their standard deviation[20].

2.5 SEM analysis

In order to explore the heterogeneity of the SRM 1648a, a sample of the reference material was studied using a Scanning Electronic Microscope (SEM JSM- 6060LV, JEOL) operated at 20 KV at Centro de Física Avanzada y Teconología Aplicada, UNAM. The images were obtained with a backscattered detector and the elemental composition of the sample was determined by energy dispersive X-ray spectroscopy (EDS) using a microanalyzer (Oxford Inca X-Sigh) coupled to the microscope.

3. RESULTS AND DISCUSSION

3.1 Digestion of SRM 1648a using HNO_3/HF reflux

For the optimization of the dissolution method for SRM 1648a using the HNO_3/HF mixture on a hot-plate, independent samples were digested from 1 to 14 days to assess the effect that reaction time can have upon elemental recoveries. Fig. 1 shows the measured concentration of selected elements in SRM 1648a *vs.* reflux time. The typical behavior for most elements is exemplified by V, Cu, Sr, and Pb. Our results suggest that more than 90% of the recoverable element leaches off the SRM after one-day reflux, and only slights improvements on the recoveries are obtained after a four-day reflux. In contrast, Cr recoveries improve by digesting the SRM for up to eight days in acid reflux, but very low recoveries are observed even after 14 days on the hot-plate. Our results also indicate that Zr recoveries, though consistently low, are negatively affected by the reflux-time, suggesting that this element might be easily liberated from the original matrix, but further reaction time might lead to its loss, probably via precipitation of ZrO_2. In general, the results in Fig. 1 indicate that a 4-day reflux guarantees a maximum recovery for most elements of interest in SRM 1648a using a HNO_3/HF mixture.

Because elemental recoveries are essentially independent of reflux time after four days, we averaged the measured concentrations from experiments with reflux time of 4 or more days (see Table 3). Percent recoveries were calculated using the certified concentrations from the SRM 1648a CoA[16]. For non- certified elements, we compared our results to those obtained from the Geochemical and Environmental Reference Materials database (GeoReM) of the Max Plank Institute[21], which lists published analytical data for SRM 1648 and SRM 1648a. Compiled concentrations, as well as the minimum and maximum concentrations, reported in GeoReM are included in Table 3, and attests for the large variability that exists in the measurement of some elements (for example Mg, Fe, Cr, Rb). Fig. 2 compares experimental *vs.* reported concentrations for all the elements of interest, also showing the range of reported and measured concentrations by GeoReM and this work.

It is important to note that SRM 1648a was certified using analytical techniques (XRF, INAA and SS-ETV) that, in contrast to ICP-MS, are essentially unaffected by the chemical form of the element and, to a lesser degree on the mineralogical composition of the sample. Consequently, the very large variability in the data obtained from the GeoReM database for certified and non-certified elements can probably be attributed to the complexity of the SRM 1648a matrix and the variable efficiencies that different methods have for leaching/dissolving the different trace elements, as discussed in section 3.4.

Results shown in Table 3 and Fig. 2 demonstrate acceptable recoveries for most of the certified elements, with the exception of Cr (46%). Very low recoveries with respect to non-certified values were also found for Zr and Nb (34% and 64%, respectively). In addition, recoveries for Mg, Al, and Ce are relatively low (69%, 77%, and 75%, respectively). Very low Cr recoveries for SRM 1648(a) have been previously observed[8-11] and attributed to the association of Cr with mineral phases that are difficult to digest such as carbonaceous material[22], refractory minerals such as chromite[23], or insoluble spinel oxides[24]. Similarly, the low recovery for Zr, Nb, can be attributed to their presence in refractory mineral phases, such as zircon and niobiates, which usually require dissolution by more aggressive and complex digestion methods[25,26]. On the other hand, low recoveries for Mg, and Ce are probably affected by the formation of fluoride precipitates which are removed during the centrifuge step[10]. Moreover, the loss of volatile compounds of Cr, Mg and Al in the presence of HF cannot be ruled out[27].

3.2 Digestion of SRM 1648a using alternative methods

We compared the results obtained using the HNO_3/HF mixture over a hot-plate with the concentrations obtained using other digestion methods which included the use of other acid mixtures and microwave-assisted digestion (see Table 1). Results of such comparison are shown in Fig. 3. Data points away from the 1:1 line by more than 20% are labeled in the figure to highlight the differences in efficiency of the digestion method. Fig. 3 shows that, in general, the use of microwave digestion instead of a hot-plate, or addition of $HClO_4$ or H_2O_2 does not improve dissolution of SRM 1648a, as elemental recoveries are similar to those obtained using only HNO_3/HF. We note, however, that the use of the EPA recommended method (HNO_3/HCl) systematically yields lower recoveries than any of the other digestion procedures, and only Mn, Ni, Cu, Zn, As, Mo, Cd, and Pb are similar to those obtained using HNO_3/HF, which can be explained by the inability to dissolve silicates using this mixture[13,28].

Microwave-assisted digestion slightly improves the recovery of Mo, Sn, and Zr; although the recoveries for Mo and Sn were already above 80% (compared to non-certified values), and Zr recoveries using microwave digestions are still much lower than those reported in the GeoREM database.

Addition of H_2O_2 to the HNO_3/HF mixture lead to reduced recoveries for several elements (Se, Ce, Ga, Co, La, As, Ba, Pb, V) but improved de recovery of Mg and Co, whilst the rest of the elements was essentially unaffected. The lower recoveries in the presence of H_2O_2 might be explained by the precipitation of insoluble oxides, such as CeO_2, Ga_2O_3, and sulfates, such as $BaSO_4$ and $PbSO_4$ which might be lost during the centrifugation step. The recovery of the rest of the elements with the addition of H_2O_2 was not improved, which is consistent with previous observations[10].

The addition of $HClO_4$ to the HNO_3/HF mixture increases the temperature of the reflux due to the higher boiling point of $HClO_4$, and, potentially, enhances sample digestion. However, we only observe improved dissolution of Ga and Ti, which were already above 80% recovery using the HNO_3/HF mixture. Most elements are, essentially, unaffected by the addition of $HClO_4$, and only Zr recovery is slightly lower than the HNO_3/HF mixture.

The above results show that the HNO_3/HF mixture on a hot-plate already provides satisfactory recoveries for the analysis of SRM 1648a. Furthermore, the addition of $HClO_4$ or H_2O_2 or the use of microwave-assisted digestion appear to be rather innocuous to the complex matrix of SRM 1648a, yielding only minimal improvements in the recoveries.

3.3 Digestion of ambient PM samples

It would be desirable to assess the efficiency of the different dissolution methods, as tested above for SRM 1648a, on real PM samples (airborne particles collected on filters) and to verify that their digestion performance is similar to that observed with SRM 1648a. This represents a complex task, due to the difficulty in obtaining a reference material for airborne PM collected on filters, and hence, determining absolute elemental recoveries. Still, it is possible to assess the relative efficiency of the different digestion methods and their reproducibility by dissolving chemically identical ambient PM samples, collected simultaneously at the same site and under the same sampling conditions.

Using the triplicate ambient PM samples (described in section 2.2), we tested the HNO_3/HF reflux method and compared to HNO_3/HF/$HClO_4$, and HNO_3/HCl mixtures in reflux, and HNO_3/HF using the microwave system. Due to the poor performance with SRM 1648a, H_2O_2 was not added to any of the filter samples. For each triplicate sample, we treated two filters with the same digestion method to assess reproducibility, whilst the third filter was digested using a different method for comparison purposes. For each one of the five triplicate samples, at least one filter was digested using the HNO_3/HF mixture in reflux. These experiments allowed us to establish that, for identical samples digested with the same method, the difference in elemental concentrations was less than 9%, indicating that the digestion methods show very good reproducibility.

Fig. 4 compares the measured elemental mass (in ng) for each of the five samples, determined with alternative methods *vs.* HNO_3/HF reflux. Data points which differ from the 1:1 line by more than 30% are highlighted in the figure. A larger uncertainty range is used in this figure in comparison with Fig. 3 due to the additional sources of uncertainty introduced by small differences in the collection procedures. For example, although the samplers were collocated side by side, slight differences in flow-rate calibration or sampled air parcel might generate differences that accumulate on top of the analytical uncertainties.

Results in Fig. 4 indicate that the HNO_3/HF mixture on a hot-plate produces recoveries that are as good or better as any other method tested, and only Cr recovery was improved by addition of $HClO_4$. In contrast, using microwave-assisted digestion yielded lower recoveries for Ga, Co, Cu, Mo, Zn and Cr; a lower mass of Se was obtained when using $HClO_4$; and the HNO_3/HCl mixture yielded lower recoveries for Zr, Cr, Al, Mo, Ni, and V. It is important to note that the differences observed in the digestion efficiency of the real samples are not consistent with those obtained for the digestion of SRM 1648a. As it is further discussed in section 3.5, this observation might be explained by the differences in matrix, particle size, and composition between the airborne PM and SRM samples.

3.4 Elemental recovery in SRM 1648(a)

The large variability found in elemental concentrations of SRM 1648(a) reported in the GeoReM database, as well as the results described above, suggests that the SRM 1648(a) has a complex matrix which poses a challenge for its analysis. The complex matrix is probably the result of heterogeneities at a micron scale; i.e. the presence of different phases (organic and inorganic) within regions that span only several micrometers. This heterogeneity is not reflected on the homogeneity assessment described in the SRM CoA. In general, heterogeneity is not a desirable characteristic in samples because the optimum digestion method for a given element, depends on the identity of the element and the matrix that needs to be destroyed for its dissolution; hence, the optimal method for one element might imply a reduced dissolution efficiency for another[26]. The presence of metallic grains, mixed with recalcitrant organic compounds, ceramic and geological material imposes significant constrains on an optimal digestion procedure. For example, it is well known that for the analysis of geological samples the dissolution of Cr, Ni, Zr, and Nb requires aggressive methods (such as fusion or the use of high-pressure vessels during several days), which also promotes the evaporation of Zn, Cs, and Pb, leading to poor recoveries for these elements[25]. In contrast, analysis of trace elements in organic matrices usually requires either dissolution of the matrix using organic solvents, or intensive oxidation using H_2O_2 or $HClO_4$ which can lead to the loss of Ce, Cr, Pb, through the precipitation of their corresponding oxides or more complex materials, along with the potential adsorption of other trace elements to such solid phases. Moreover, recoveries can also be sensitive to the metal speciation within the sample. Under this light, the differences observed in the elemental dissolution of SRM 1648a with different digestion methods are probably a reflection of the complex heterogeneous matrix that needs to be destroyed in order to dissolve the elements.

In order to explore the micron-scale heterogeneity of the SRM 1648a matrix, we show a SEM image in Fig. 5, along with the mass concentration of selected elements for five different spots within a 30 μm^2-area. The diversity in morphology and chemical composition is evident in the image, and differences in composition ranging from 10 to 100% in concentration of some of the elements shown can be found between spots that are less than 10 μm apart from each other.

An important implication of the micron-scale heterogeneity and complexity of the SRM 1648a matrix is the fact that the recoveries obtained for certified elements might not be automatically assumed to be similar for the rest of the non-certified elements, a common practice found in the literature without further discussion. The extrapolation of conclusions made only from certified elements to the rest of the elements should be done with caution, and taking into account possibly large uncertainties due to the differences in chemical and mineralogical form of the different elements.

3.5 SRM 1648(a) as reference material for PM

As discussed above, SRM 1648(a) is usually used as a reference material for airborne aerosols, although composition and particle size distribution in both might be significantly different. For example, Al, Ca, Fe, K, Mg concentrations in SRM 1648(a) range between 0.6 to 6 %. Most of these elements, when found in airborne particles, are usually related to crustal origin. At the same time, the size distribution (expressed in volume) of the SRM 1648(a) shows only one mode with maximum size around 20 μm, which supports the above assumption that there is a large contribution of crustal material in the SRM 1648(a) because large particles are usually produced by mechanical processes such as wind or erosion. In urban areas instead, the total PM mass contains only a small fraction of crustal elements. Fine particles are usually formed by combustion processes, as well as nucleation, condensation growth or coagulation of smaller particles, and they are usually composed of nitrate, sulfate, ammonium, organic compounds, elemental carbon, and trace elements contained in fuels. Furthermore, the size distribution of ambient airborne particles usually shows two modes: a fine mode with maximum size below 1 μm, and a coarse mode with maximum size below 10 μm[29]. In fact, airborne samples collected for atmospheric studies are usually PM_{10}, $PM_{2.5}$, or even PM_1, which are the more relevant PM fractions for Air Quality Standards, and because the smallest particles have the largest health effects. Another example of an specific difference between SRM 1648(a) and airborne PM is the Pb content, which in the SRM 1648(a) is 0.655%, while in current urban $PM_{2.5}$ is not larger than 0.2% and even less, as shown in several studies chosen as examples[30-34]. The difference might be a reflection of the fact that leaded gasoline was still in use during the collection of the SRM 1648(a) (1976-1977)[35]. Hence, the size distribution and chemical composition of SRM 1648(a) suggests that airborne particles might have a different matrix to be digested, which might translate into differences in the digestion efficiencies of some elements (as discussed in section 3.4). The complex matrix and micro-scale heterogeneity shown above, could also have an effect on elemental recoveries because some particles might be prevented to be in contact with the acidic-mixture if they are covered by aggregation of other particles of different nature (e.g. recalcitrant and/or hydrophobic organic material); such particles could not react with the acidic mixture causing low-recoveries.

The differences in chemical composition and particle size between airborne PM and SRM 1648a, as well as the effects of the matrix on dissolution efficiency, might explain the inconsistencies in the relative recoveries when using different digestion methods described in section 3.3.

It is common practice in the literature to extrapolate the results obtained with SRM 1648(a) to real PM samples collected on filters without further discussion. However, same as non-certified elements (see section 3.4), the extrapolation of SRM 1648(a) results to real PM samples might introduce unknown uncertainties in the elemental recoveries in airborne PM. Such uncertainties might vary depending on the sampling site and time because chemical composition of atmospheric aerosols is highly variable. Hence trace element concentrations in PM determined by acidic dissolution followed by ICP-MS measurements probably have relative large uncertainties. Therefore, it would be important to further investigate the dissolution of real airborne PM samples collected in varying environments in order to better quantify such uncertainties.

As mentioned before, in general atmospheric composition measurements have relatively large uncertainties[17-19], without reducing their worth to understanding atmospheric chemical processes. Thus, this study does not intend to invalidate the use of any digestion method for the determination of trace elements in PM. On the contrary, it attempts to shed some light on their uncertainties, which might be helpful for the interpretation of atmospheric data.

4. CONCLUSIONS

We tested a digestion method using acid reflux over a hot plate in a mixture of HNO_3/HF for the elemental dissolution of SRM 1648a before ICP-MS analysis. The method yields acceptable recoveries for most of the certified elements (Ti, V, Mn, Fe, Ni, Co, Cu, Zn, As, Rb, Sr, Cd, Pb), with few exceptions (Mg, Al, Cr, and Ce). The use of a microwave system to assist digestion and the addition of $HClO_4$ or H_2O_2 does not improve the recoveries, whilst the use of HCl instead of HF results in poorer recoveries for many elements. Several non-certified elements were also analyzed in this study (Ga, Se, Zr, Nb, Mo, Sn, Sb, Cs, Ba, La, Nd, Sm, Th, The and U), and the recoveries for most of them are in line to prior reports, with the exception of Zr, whose determination is usually not reported.

The same digestion method was tested on real PM samples collected on PTFE filters. Although the efficiency of the dissolution cannot be determined, its reproducibility lies within 9%.

In general it is assumed that the elemental recoveries determined for certified elements in SRM 1648(a) can be directly extrapolated to non-certified elements in the reference material and to airborne particles. However, we showed that uncertainties related to this assumption are not well characterized due to a very heterogeneous matrix and differences in particle size and chemical composition of the SRM 1648(a) *vs.* real samples. The uncertainties might become especially evident when comparing trace elements data from different sites with dissimilar PM sources and composition. Hence, it would be important to further investigate the dissolution of real airborne PM samples collected in varying environments in order to better quantify such uncertainties.

ACKNOWLEDGMENTS

We are grateful to Carolina Muñoz-Torres (Centro de Geociencias, UNAM) for her help with the microwave digestions, and Marina Vega (Centro de Geociencias, UNAM) for the SEM analysis. Funding was provided by CONACyT Mexico (project CB-2009/133696) and the Molina Center for Energy and the Environment in La Joya CA, USA.

REFERENCES

1. IPCC, *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, 2007*, Cambridge University Press, 2007.
2. P. N. Breysse, R. J. Delfino, F. Dominici, A. C. P. Elder, M. W. Frampton, J. R. Froines, A. S. Geyh, J. J. Godleski, D. R. Gold, P. K. Hopke, P. Koutrakis, N. Li, G. Oberdörster, K. E. Pinkerton, J. M. Samet, M. J. Utell, and A. S. Wexler, *Air Qual. Atmos. Heal.*, 2012, **6**, 333–355.
3. US EPA, *Particulate Matter (PM2.5) Speciation Guidance, Final Draft*, U.S. Environmental Protection Agency, Research Triangle Park, 1999.
4. M. Lippmann, *J. Expo. Sci. Environ. Epidemiol.*, 2009, **19**, 235–47.
5. M. Franklin, P. Koutrakis, and J. Schwartz, *Epidemiology*, 2008, **19**, 680–689.
6. P. A. Solomon, G. Norris, M. Landis, and M. Tolocka, in *Aerosol measurement. Principles, techniques, and applications*, eds. P. A. Baron and K. Willeke, John Wiley & Sons, Canada, 2001, pp. 261–294.

7. US EPA, *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air*, Washington DC, 1999.

8. J. Niu, P. E. Rasmussen, and M. Chénier, *Int. J. Environ. Anal. Chem.*, 2013, **93**, 661–678.

9. N. J. Pekney and C. I. Davidson, *Anal. Chim. Acta*, 2005, **540**, 269–277.

10. P. Kulkarni, S. Chellam, J. B. Flanagan, and R. K. M. Jayanty, *Anal. Chim. Acta*, 2007, **599**, 170–176.

11. K. Swami, C. D. Judd, J. Orsini, K. X. Yang, and L. Husain, *Fresen. J. Anal. Chem.*, 2001, **369**, 63–70.

12. V. Celo, E. Dabek-zlotorzynska, D. Mathieu, and I. Okonskaia, *Open Chem. Biomed. Meth. J.*, 2010, **3**, 143–152.

13. N. M. Hassan, P. E. Rasmussen, E. Dabek-Zlotorzynska, V. Celo, and H. Chen, *Water Air Soil Poll.*, 2006, **178**, 323–334.

14. P. Smichowski, D. Gomez, and G. Polla, *Curr. Anal. Chem.*, 2005, **1**, 373–394.

15. P. Smichowski, D. Gómez, C. Frazzoli, and S. Caroli, *Appl. Spectrosc. Rev.*, 2007, **43**, 23–49.

16. S. A. Wise and R. L. Watters, *Standard Reference Material 1648a, certificate of analysis.*, Gaithersburg, MD, 2008.

17. D. Salcedo, A. Laskin, V. Shutthanandan, and J. L. Jimenez, *Aerosol Sci. Technol.*, 2012, **46**, 1187–1200.

18. N. Takegawa, Y. Miyazaki, Y. Kondo, Y. Komazaki, T. Miyakawa, J. L. Jimenez, J. T. Jayne, D. R. Worsnop, J. D. Allan, and R. J. Weber, *Aerosol Sci. Technol.*, 2005, **39**, 760–770.

19. I. C. Rumsey, K. A. Cowen, J. T. Walker, T. J. Kelly, E. A. Hanft, K. Mishoe, C. Rogers, R. Proost, G. M. Beachley, G. Lear, T. Frelink, and R. P. Otjes, *Atmos. Chem. Phys. Discuss.*, 2013, **13**, 25067–25124.

20. IUPAC, *Compendium of Chemical Terminology*, Blackwell Scientific Publications, Oxford, 2006.

21. K. P. Jochum, U. Nohl, K. Herwig, E. Lammel, B. Stoll, and A. W. Hofmann, *Geostand. Geoanal. Res.*, 2005, 333–338.

22. L. M. Jalkanen and E. K. Hasanen, *J. Anal. At. Spectrosc.*, 1996, **11**, 365–369.

23. T. Yamashige, M. Yamamoto, and H. Sunahara, *Analyst*, 1989, **114**, 1071–1077.

24. O. T. Butler and a M. Howe, *J. Environ. Monit.*, 1999, **1**, 23–32.

25. V. Balaram, S. L. Ramesh, and K. V Anjaiah, *Anal. Bioanal. Chem.*, 1995, **353**, 176–82.

26. T. T. Chao and R. F. Sanzolone, *J. Geochem. Explor.*, 1992, **44**, 65–106.

27. C. F. Wang, W. H. Chen, M. H. Yang, and P. C. Chiang, *Analyst*, 1995, **120**, 1681–1686.

28. V. L. Mateus, I. L. G. Monteiro, R. C. C. Rocha, T. D. Saint'Pierre, and A. Gioda, *Spectrochim. Acta Part B At. Spectrosc.*, 2013, **86**, 131–136.

29. J. H. Seinfeld and S. N. Pandis, *Atmospheric chemistry and physics*, John Wiley and Sons, Hoboken NJ, 2nd edn., 2006.

30. L. Xu, Y. Yu, J. Yu, J. Chen, Z. Niu, L. Yin, F. Zhang, X. Liao, and Y. Chen, *Sci. Total Environ.*, 2013, **442**, 77–85.

31. X. Querol, J. Pey, M. C. Minguillon, N. Pérez, A. Alastuey, M. Viana, T. Moreno, R. M. Bernabé, S. Blanco, B. Cérdenas, E. Vega, G. Sosa, S. Escalona, H. Ruiz, and B. Artíñano, *Atmos. Chem. Phys.*, 2008, **8**, 111–128.

32. C. Pio, F. Mirante, C. Oliveira, M. Matos, A. Caseiro, C. Oliveira, X. Querol, C. Alves, N. Martins, M. Cerqueira, F. Camões, H. Silva, and F. Plana, *Atmos. Environ.*, 2013, **71**, 15–25.

33. G. Argyropoulos, E. Manoli, A. Kouras, and C. Samara, *Sci. Total Environ.*, 2012, **432**, 12–22.

34. P. Smichowski, D. R. Gómez, L. E. Dawidowski, M. F. Giné, A. C. S. Bellato, and S. L. Reich, *J. Environ. Monit.*, 2004, **6**, 286–94.

35. US EPA, EPA Requires Phase-Out of Lead in All Grades of Gasoline, EPA press release November 28, 1973.

TABLES AND FIGURES

Table 1. Digestion methods tested with SRM 1648a samples.

acid mixture	digestion method		number of samples
3 mL HNO_3 + 0.3 mL HF	reflux 100 - 120^{o}C	14 days	1
		9 days	1
		8 days	1
		7 days	5
		6 days	1
		4 days	4
		1 day	1
3 mL HNO_3 + 0.3 mL HF + 5 drops H_2O_2 before final evaporation	reflux 100 - 120^{o}C	7 days	1
0.2 mL HNO_3 + 0.6 mL HCl + 2.8 mL H_2O	reflux 100 - 120^{o}C	1 hour	1
	reflux 100 - 120^{o}C	1 day	2
3 mL HNO_3 + 0.3 mL HF + 0.3 mL $HClO_4$	reflux 100 - 120^{o}C	4 days	2
3 mL HNO_3 + 0.3 mL HF	microwave		3

Table 2. Instrumental parameters for the Thermo X-series II

RF power (W)	1300
Sample depth (mm)	1
Nebulizer gas (L min^{-1})	0.84
Nebulizer pumps (rps)	0.25
Dwell time (ms)	40

Table 3. Limits of detection (LOD) for the elements studied. Reported concentrations in SRM 1648a (NIST CoA[16] and GeoReM[21]), average measured concentrations (standard deviation in parenthesis), and elemental recoveries using acid-reflux (HNO_3/HF) for at least 4 days. Mean, minimum and maximum concentrations reported in GeoReM are included.

	LOD (μg/g)	concentration in SRM 1648a (μg/g)					% recovery
		NIST certified	NIST reference and GeoReM	minimum GeoReM	maximum GeoReM	this work	
Mg	12	8130		2100	8900	5597 (943)	69%
Al	7.8	34300		27600	38000	26352 (3269)	77%
Ti	4.5	4021		3100	4700	3386 (302)	84%
V	0.89	127		91	160	102 (7)	80%
Cr	2.2	402		236	430	184 (38)	46%
Mn	3.2	790		651	894	685 (54)	87%
Fe	6.4	39200		14500	41700	32190 (3472)	82%
Ni	3.6	81		62	103	83 (10)	102%
Co	0.12	18		13	19	14 (2)	79%
Cu	2.5	610		491	656	477 (39)	78%
Zn	5.1	4800		3672	6580	4154 (735)	87%
Ga	0.23		36[a]	18	55	32 (6)	
As	3.1	116		82	160	102 (6)	88%
Se	4.3		28[b]	12.9	31.7	21 (2)	
Rb	3.5	52		20.2	57	44 (3)	84%
Sr	0.55	215		144	230	187 (9)	87%
Zr	0.85		177[a]	164	190	61 (16)	
Nb	0.21		26[a]	26	NA	17 (6)	
Mo	0.92		14[a]	5.0	15	14 (3)	
Cd	0.36	74		41	87	65 (5)	88%
Sn	0.47	NA	NA	NA	NA	85 (13)	
Sb	0.11		45[a]	27	65	34 (6)	
Cs	0.12		3.4[b]	1.4	3.3	2.8 (0.2)	
Ba	1.3		698[a]	546	816	577 (52)	
La	0.15		39[b]	32	39	28 (4)	
Ce	0.16	55		45	58	41 (4)	75%
Nd	0.17		25[a]	23.5	27	21 (3)	
Sm	0.13		4.3[b]	1.5	4.2	3.5 (0.4)	
Pb	1.8	6550		4470	7270	5689 (554)	87%
Th	0.25		6.2[a]	0.67	7.3	6.0 (0.7)	
U	0.07		5.1[a]	3.1	5.8	4.9 (0.5)	

a. GeoReM; b. NIST reference values.

Fig. 1. Measured concentration (µg/g) in SRM 1648a for selected elements *vs.* reflux time in HNO_3/HF mixture. Grey lines correspond to the reported concentration (NIST certified values[16] for V, Cr, Cu, Sr, and Pb; GeoReM mean value[21] for Zr).

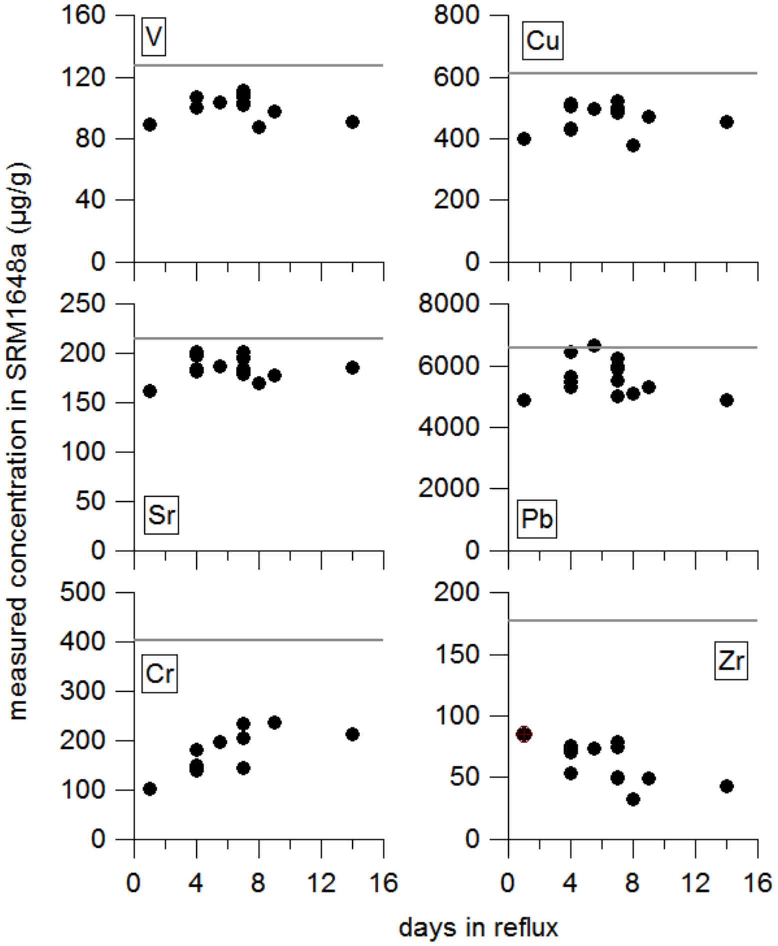


Fig. 2. Averaged experimental elemental concentrations (HNO_3/HF reflux for at least 4 days) *vs.* reported concentrations in SRM 1648a. Red bars include minimum and maximum concentrations measured; black bars include the minimum and maximum concentrations reported in GeoReM. The black line corresponds to a 1:1 line and the grey area represents a 20% uncertainty; they are shown only as a visual reference.

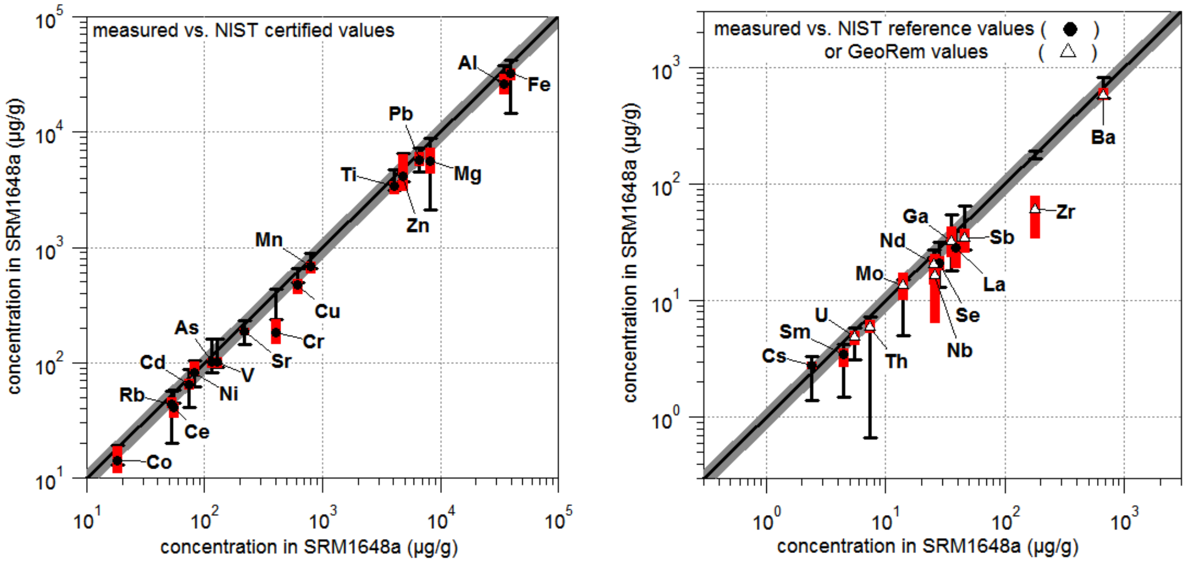


Fig. 3. Elemental concentration measured using alternative digestion methods *vs.* HNO_3/HF reflux. 1:1 lines are shown for visual reference. Red markers represent elements that are within 20% of the 1:1 line; the rest of the elements are represented with larger black markers and labeled.

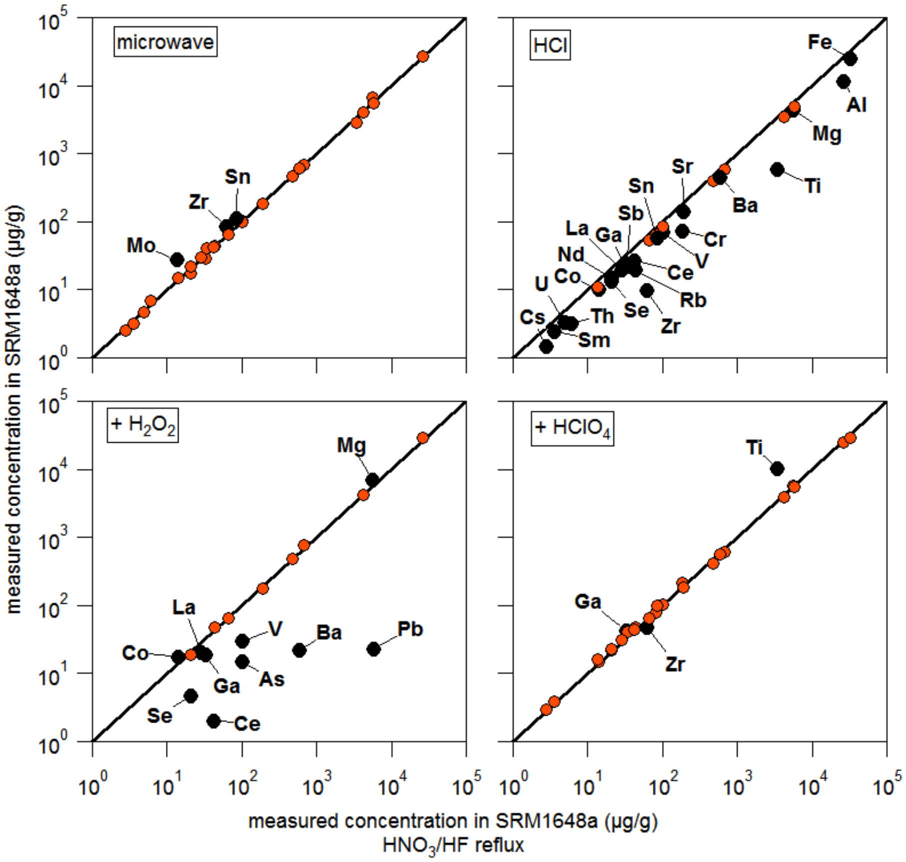


Fig. 4. Elemental mass measured in triplicate PM samples on PTFE filters, using alternative digestion methods *vs.* reflux in HNO_3/HF. 1:1 lines (black solid lines) are shown for visual reference. Bars are minimum and maximum concentrations measured in two duplicated samples using the same method. Red markers represent elements that are within 30% of the 1:1 line; the rest of the elements are represented with larger black markers and labeled.

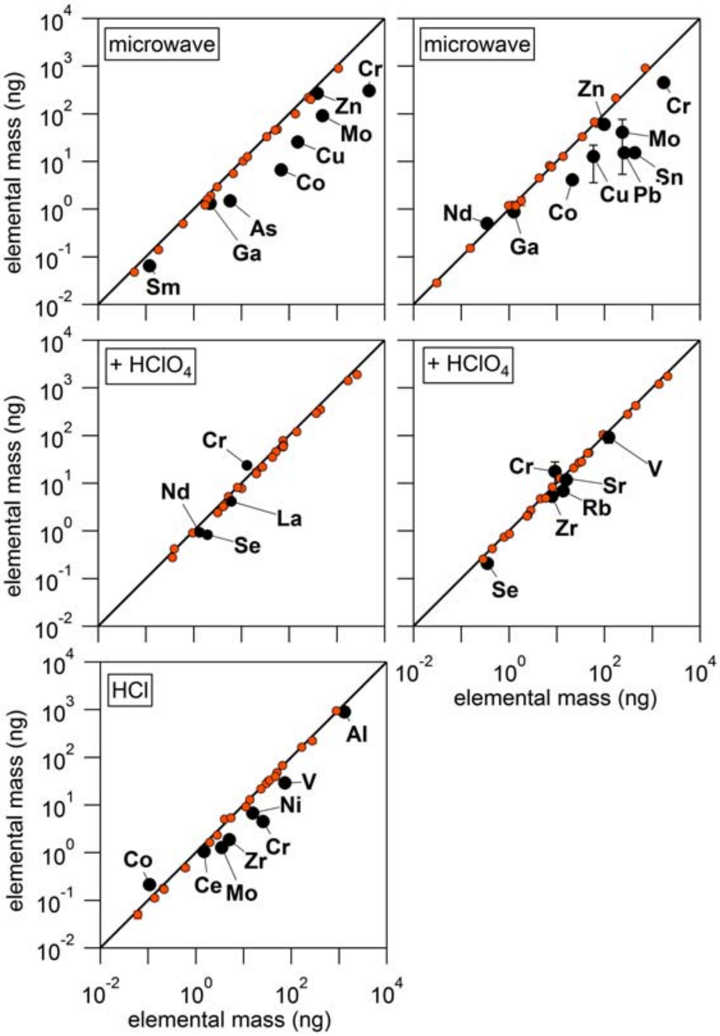
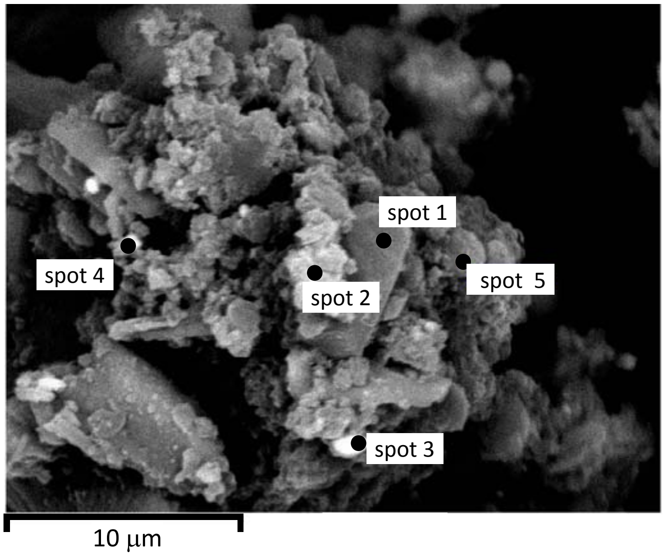


Fig. 5. SEM image of a SRM 1648a sample and results from the EDS analysis (in wt%) for five spots in the sample.



	1	**2**	**3**	**4**	**5**
C	62.5	51.4	61.3		16.5
Na	0.38				3.35
Mg		0.8	0.44		1.93
Al	0.32	0.61	0.52	3.15	3.13
Si	2.44	2.01	1.37		8.85
K	0.17	0.2	0.29	3.14	
Ca	0.23	0.38	1.04	4.22	0.65
Fe	0.76	0.65	0.61	3.85	
Zr	0.84			7.02	
Pb			0.92	10.0	