Talanta 97 (2012) 63–72

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Survey analysis and chemical characterization of solid inhomogeneous samples using a general homogenization procedure including acid digestion, drying, grinding and briquetting together with X-ray fluorescence

Eskil Sahlin*, Bertil Magnusson

SP Technical Research Institute of Sweden, Brinellgatan 4, SE-501 15 Borås, Sweden

ARTICLE INFO

Article history:
Received 11 November 2011
Received in revised form
10 March 2012
Accepted 24 March 2012
Available online 21 May 2012

Keywords:
Survey analysis
Chemical characterization
X-ray fluorescence
Homogenization
Digestion

ABSTRACT

A survey analysis and chemical characterization methodology for inhomogeneous solid waste samples of relatively large samples (typically up to 100 g) using X-ray fluorescence following a general homogenization procedure is presented. By using a combination of acid digestion and grinding various materials can be homogenized e.g. pure metals, alloys, salts, ores, plastics, organics. In the homogenization step, solid material is fully or partly digested in a mixture of nitric acid and hydrochloric acid in an open vessel. The resulting mixture is then dried, grinded, and finally pressed to a wax briquette. The briquette is analyzed using wave-length dispersive X-ray fluorescence with fundamental parameters evaluation. The recovery of 55 elements were tested by preparing samples with known compositions using different alloys, pure metals or elements, oxides, salts and solutions of dissolved compounds. It was found that the methodology was applicable to 49 elements including Na, Mg, Al, Si, P, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Ta, W, Re, Ir, Pt, Au, Tl, Pb, Bi, and Th, that all had recoveries >0.8. 6 elements were lost by volatilization, including Br, I, Os, and Hg that were completely lost, and S and Ge that were partly lost. Since all lanthanides are chemically similar to La and Ce, all actinides are chemically similar to Th, and Hf is chemically similar to Zr, it is likely that the method is applicable to 77 elements. By using an internal standard such as strontium, added as strontium nitrate, samples containing relatively high concentrations of elements not measured by XRF (hydrogen to fluorine), e.g. samples containing plastics, can be analyzed.

1. Introduction

Our surroundings today consists of a vast number of products and objects that are each made of many different materials. Many of these products and materials will end up as waste in different forms after disposal. Some of these materials are highly precious and hence there is an emerging interest in recycling some of the materials in the waste [1,2]. For instance, within the framework of the EU Raw Materials Initiative several raw materials have been classified as being of high relative economic importance and several materials have been classified as having a relatively high supply risk [1,3]. In order to secure access to these materials, increased recycling of materials is one of the recommended strategies [1]. In order to study material flow in wastes and make decisions regarding waste treatment and possible recycling of elements and materials, chemical characterization and survey analysis techniques are needed in order to estimate the amount of different elements.

Elemental survey analysis of waste is however a challenging task. Waste samples are typically inhomogeneous and consist of mixtures of many different materials and compounds that are often totally unknown. Elements of interest can be present in different forms such as elemental, or as oxides or salt, or incorporated into a plastic matrix. In addition, analytical procedures that can handle this, and that are both quantitative and capable of measuring most of the elements in the periodic table are needed. To the best of our knowledge, survey analysis and chemical characterization of different types of waste is rarely described in the literature. The only alternative is large sample activation methods that have been developed to handle samples in the kg range [4].

In order to develop a method for general elemental characterization of inhomogeneous material all elements of interest (about 80 elements in total) should be quantified. Techniques for quantitative elemental analysis covering a major part of

---

* Corresponding author. Tel.: +46 10 516 52 65; fax: +46 33 12 37 49.
E-mail addresses: eskil.sahlin@sp.se (E. Sahlin), bertil.magnusson@sp.se (B. Magnusson).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.03.063

these elements are neutron activation analysis (NAA), X-ray fluorescence (XRF), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and inductively coupled plasma–mass spectrometry (ICP–MS). All these techniques can be used both for liquid and solid samples but the ICP techniques for solid sampling, laser ablation, is not quantitative. In order to use the ICP techniques a dissolution or digestion of the solid sample into a liquid sample is required. However digestion is difficult since a general dissolution procedure for solid samples is not to our knowledge available. Compared to NAA, XRF is more available and the multielement capability of XRF is excellent and the only drawback is that some light elements cannot be reliably quantitatively measured.

For the sample preparation the following issues have to be taken into account. An unknown waste sample can consist of a vast number of parts that contain elements present as pure metals, salts, oxidic samples, plastics, organics of biological origin etc. In order to reliably analyze inhomogeneous samples with XRF it is necessary to homogenize the samples and preferably reduce the particle size to μm size in order that the surface layer analyzed represents the bulk sample. There are several approaches to homogenize a solid test sample in order to get it more suitable for accurate XRF analysis including remelting of metallic samples, fusion of oxidic samples [5,6], fusion of metallic samples after acid digestion [5], and grinding [6]. Remelting is commonly used for pure metals in order to homogenize the sample but it is not general applicable. Fusing into a glass bead works well for most oxidic samples, and if the sample to be fused contains metals; the most metallic part can be dissolved by acid digestion prior to fusion or preoxidised using nitrate as the first step in the fusion procedure. However, several elements are problematic since some elements will volatilize or alloy with the dish [6] and it is difficult to have a general procedure for all elements. Many materials can be grinded in a swing-mill using tungsten carbide (e.g. oxide compounds of geological origin) or cut (plastics) [6] but this is not applicable to metals. Hence, if the matrix is known, sample preparation may be developed and optimized for that type of matrix. For samples with unknown matrix containing e.g. oxides, metallic components, salts, plastics, and organic matter none of the above discussed sampling preparation procedures can handle all these different components. In order to handle these difficulties we propose a combination of grinding and acid digestion of metallic parts that are not possible to grind.

Hence, the scope of this work is to address the difficulties with elemental survey analysis and chemical characterization of inhomogeneous relatively large test samples (100 g) having unknown composition by using wavelength dispersive XRF capable of analyzing up to 70 elements, together with a sample homogenization procedure where grinding and acid digestion is combined.

2. Materials and methods

2.1. Chemicals and materials

Nitric acid and hydrochloric acid (p.a. grade) were obtained from Merck (Germany).

Certified reference alloys BCS 181/3, BCS/SS 310/1, BCS/SS no. 345 (British chemical standards) were from Bureau of Analysed Samples, Ltd. Middlesbrough (England), and IPT Amostra Padro 10 A was from Instituto de pesquisas technológicas, Sao Paolo (Brazil). Aluminum (> 99%), cadmium, copper (> 99.7%), gold (> 99.5%), iron (> 99.5%), and selenium (> 99.5%) were obtained from Merck. Antimony (> 98.5%) was obtained from BDH Chemicals Ltd. (Poole, England) and bismuth was obtained from ROTH (Karlsruhe, Germany).

Arsenic trioxide, barium carbonate, calcium chloride dihydrate, potassium chloride, potassium dihydrogen phosphate, sodium bromide, sodium chloride, sodium sulfate, strontium nitrate, thallium nitrate, and zircon(IV)-oxidchloride octahydrate (all p.a. grade), rubidium chloride (> 99.5%), and yttrium chloride hexahydrate (> 99%), were obtained from Merck. Sodium iodide (98%) was obtained from Sigma-Aldrich and cesium chloride (> 99.5%) was obtained from Shelton Scientific Inc. (Shelton, CT, USA).

Multielement standard (solution) containing Au, Ir, Os, Pd, Pt, Re, Rh, and Ru (100 mg L^{-1}), and single element standards containing Ag (1000 mg L^{-1}) and Rh (1000 mg L^{-1}) were obtained from Spectrascan (Kungsbacka, Sweden). Single element standards containing Ir, Pd, and Sc (all 1000 mg L^{-1}) were obtained from Referensmaterial AB (Ulricehamn, Sweden). Single element standards containing Ga, Ge, Hg, Pt, and Te (all 1000 mg L^{-1}) were obtained from Ultra Scientific (Kingstown, RI, USA). Single element standards containing In, Nb, Ta, Th, and W (all 1000 mg L^{-1}) were obtained from High Purity Standard (Charleston, SC, USA).

Poly(methyl methacrylate) (PMMA) and fire steel (Swedish FireSteel Scout from Light My Fire, Malmö, Sweden) were purchased in a local hardware store. Fire steel was used as a source for Ce and La and the assigned values of the main components Ce, La, and Fe were determined by XRF (without digestion of the alloy). Silicon iron alloy (powder) was received from Elkem Solar (Oslo, Norway).

Samples with different compositions were prepared by mixing assigned reference materials of different alloys (certified reference materials and miscellaneous alloys with composition determined in the laboratory), pure elements, compounds, and elements in solutions.

Briquettes were pressed using Licowax C Micropowder PM, Hoechstwax, (Hoechst AG, Frankfurt am Main, Germany) in aluminum cups (Chemplex #500) (Chemplex Industries, Inc., Palm Springs, Florida).

2.2. Methods

2.2.1. Sample preparation

For larger primary samples (> 100 g) a subsampling procedure can applied in order to obtain a test sample of maximum 100 g. In order to study new material the sampling uncertainty can be evaluated using duplicate analyses of different batches [7]. The test samples were homogenized by acid digestion using a mixture of nitric and hydrochloric acid resulting in a slurry containing dissolved, partly dissolved and leached material that is dried and grind. The sample, typically up to 100 g, was added to a mixture of concentrated nitric acid (65%), hydrochloric acid (37%), and water in a Pyrex glass bottle (size 1 L) in the ratio 30 g sample: 100 mL nitric acid: 100 mL hydrochloric acid: 60 mL water. Portions of the test samples were added carefully in order to avoid a too vigorous acid reaction. The mixture was then boiled with a loose lid on top of the Pyrex bottle for at least an hour and then cooled to room temperature. The process resulted in a slurry of dissolved and precipitated salts, and in some cases undigested materials such as polymers. The slurry, or part of the slurry after homogenization, was then transferred to a glass beaker (diameter min 15 cm for 100 g sample) and heated on a sand bath at 120–180 °C for typically 10 h in a fume hood. After cooling to room temperature the dried material was grinded in a mortar and dried at 200 °C in an oven equipped with a ventilator for typically for 2 h. Some metals, alloys, plastics and some silicon based materials may not be digested by the described acid mixtures. If these particles are below 50 μm or can be grinded the sample is still suitable for XRF. Larger particles have to be isolated and analyzed separately by XRF. A subsample of 4.2 g of the dried material was mixed with 0.60 g wax and pressed for 3 min at a pressure of 0.18 GN/m^2 to a 32 mm briquette using aluminum cups (Chemplex #500).

In order to compensate for the amount of organic matter present in the sample, strontium was added as strontium nitrate and used as an internal standard for samples originally containing a negligible strontium concentration. Typically, 1 g strontium nitrate was added to 6 g sample.

2.2.2. *XRF measurement*

The briquette was analyzed using wavelength dispersive XRF. Analysis was performed using ARL Advant'X Intellipower^{TM} 3600 XRF Uniquantometer from Thermo Scientific and 74 elements with 114 lines given in Table 1 were measured under vacuum and the measured intensities were drift corrected and evaluated using the software UniQuant® (Thermo Scientific) supplied by the manufacture. In order to obtain high spectral resolution the peak measurements at fixed positions were optimized for spectral resolution and not for sensitivity i.e. by the choice of crystal, fine collimator, and narrow pulse height settings of the detectors. Data collection was performed with measurement of both K and L lines and several reliable background positions. The calibration was performed by the vendor using 64 standard samples for estimating the element sensitivity for the 114 measured lines and about 1500 spectral overlap corrections in order to cover varying matrices. The spectral corrections are concentration based. For element in high concentration ($>$ 10%) that can interfere with trace analytes the overlap corrections were verified by analyzing pure elements with high purity. The drift correction was applied with 9 standard samples. A general mathematical matrix correction using fundamental parameters is included in the evaluation program. Input data for evaluation of sample concentrations were 1) amount: 4.8 g, 2) sample diameter: 32 mm, 3) dilution factor for the briquette (0.6 g wax/4.2 g sample): 0.143, and 4) the elemental composition of the wax used for making the briquettes. Elements were evaluated as elements with a rest of oxygen where oxygen is calculated as 100% minus the sum of all the measured elements. The amount of oxygen is calculated by iteration. For those elements detected where two lines were measured the results for the two lines were compared. The homogeneity of the test specimen was assessed for the elements detected where both the K and the L lines were measured by a comparison of the results. The result was normalized to 100% and transferred to a spreadsheet calculation software. In the spreadsheet the chlorine results were taken out and the results were again normalized.

2.2.3. *Characterization of test specimen for samples of pure elements obtained with the sample preparation procedure*

Dried powder obtained with the sample preparation procedure from samples consisting of pure aluminum, copper and iron were characterized chemically by several analyses including ion chromatography, inductively coupled plasma-optical emission spectroscopy, and X-ray diffraction. Elemental chlorine was determined using XRF.

2.2.4. *Ion chromatography*

Water soluble chloride and water soluble nitrogen-nitrate were determined by leaching samples (0.10 g sample in 100 mL water) for 5 h and subsequent determination of chloride and nitrate in the aqueous phase using an ion chromatography system with conductivity detection (861 Advanced Compact IC from Metrohm AG, Herisau, Switzerland equipped with a Metrosep

Table 1
Measured elements and lines with the XRF instrumentation.

Element	Line	Energy (keV)	Alternative line[a]
Ba	Kα	32.04	–
Cs	Kα	30.85	–
I	Kα	28.51	–
Te	Kα	27.37	–
Sb	Kα	26.27	–
Sn	Kα	25.20	–
In	Kα	24.12	–
Cd	Kα	23.13	–
Ag	Kα	22.10	–
Pd	Kα	21.12	–
Rh	Kα	20.20	–
Ru	Kα	19.25	–
Mo	Kα	17.46	–
Nb	Kα	16.58	–
Th	Lβ	16.19	X
Zr	Kα	15.74	–
Y	Kα	14.92	–
Am	Lα	14.62	–
Pu	Lα	14.29	–
Sr	Kα	14.14	–
U	Lα	13.61	–
Rb	Kα	13.38	–
Th	Lα	12.97	–
Pb	Lβ	12.63	–
Tl	Lβ	12.22	–
Br	Kα	11.91	–
As	Kβ	11.73	–
Au	Lβ	11.45	X
Se	Kα	11.21	–
Pt	Lβ	11.07	X
Bi	Lα	10.84	–
Pb	Lα	10.55	X
As	Kα	10.54	X
Os	Lβ	10.36	–
Re	Lβ	10.02	–
Hg	Lα	9.98	–
Ge	Kα	9.87	–
Au	Lα	9.71	–
W	Lβ	9.67	X
Pt	Lα	9.44	–
Ta	Lβ	9.35	X
Ga	Kα	9.25	–
Ir	Lα	9.17	–
Hf	Lβ	9.02	–
Lu	Lβ	8.71	X
Zn	Kα	8.63	–
W	Lα	8.40	–
Ni	Kβ	8.27	X
Ta	Lα	8.15	–
Cu	Kα	8.04	–
Lu	Lα	7.66	–
Ho	Lβ	7.53	–
Ni	Kα	7.47	–
Yb	Lα	7.42	–
Dy	Lβ	7.25	–
Tm	Lα	7.18	–
Er	Lα	6.95	–
Co	Kα	6.92	–
Eu	Lβ	6.46	X
Fe	Kα	6.40	–
Tb	Lα	6.28	–
Sm	Lβ	6.21	–
Gd	Lα	6.06	–
Mn	Kα	5.90	–
Eu	Lα	5.85	–
Sm	Lα	5.64	X
Pr	Lβ	5.49	–
V	Kβ	5.43	X
Cr	Kα	5.41	–
Ce	Lβ	5.26	–
Nd	Lα	5.23	–
Pr	Lα	5.03	X
V	Kα	4.95	–
Ti	Kβ	4.93	X

Table 1 (*continued*)

Element	Line	Energy (keV)	Alternative line[a]
Ce	Lα	4.84	X
Ba	Lβ	4.83	X
La	Lα	4.65	–
Ti	Kα	4.51	–
Cs	Lα	4.29	X
I	Lβ	4.22	X
Sc	Kα	4.09	–
Ca	Kβ	4.01	X
Sb	Lβ	3.84	X
Te	Lα	3.77	X
Ca	Kα	3.69	–
In	Lβ	3.49	X
Sn	Lα	3.44	X
K	Kα	3.31	–
Ag	Lβ	3.15	X
Cd	Lα	3.13	X
Pd	Lα	2.96	X
Rh	Lα	2.84	X
Cl	Kα	2.70	–
Ru	Lα	2.62	X
Mo	Lβ	2.56	X
Sx	Kα	2.40	X
S	Kα	2.31	–
Nb	Lα	2.31	X
Zr	Lα	2.17	X
Px	Kα	2.04	X
P	Kα	2.02	–
Y	Lβ	2.01	X
Sr	Lα	2.00	X
Si	Kα	1.81	–
Br	Lβ	1.74	X
Al	Kα	1.53	–
Se	Lα	1.49	X
Mg	Kα	1.38	–
Ga	Lβ	1.25	X
Na	Kα	1.12	–
Cu	Lβ	1.04	X
Co	Lβ	0.95	X
Fe	Lβ	0.79	X
F	Kα	0.72	–

[a] Alternative line used for checking the evaluation of the results.

A Supp 5 100/4.0 mm column and 3.2 mM Na_2CO_3/1.0 mM $NaHCO_3$ as eluent).

2.2.5. *Inductively coupled plasma – optical emission spectroscopy*

Al, Cu and Fe were determined in the powder by inductively coupled plasma–optical emission spectroscopy (ICP–OES) (Optima 3000DV from Perkin Elmer, Waltham, MA, USA) after dissolution of the powder in a mixture of 50 volume-% concentrated nitric acid and 50 volume-% concentrated hydrochloric acid.

2.2.6. *X-ray diffraction measurements*

In order to determine what crystalline phases are present, the samples were analyzed with a powder diffractometer D8 Advance produced by Bruker AXS with CuKα1 radiation (40 kV, 40 mA, $\lambda=1.54056$ Å) in Bragg-Brentano geometry using curved primary monochromator and LynxEye position sensitive detector. The measurement was made using the detector scan in region 15–65° in 2θ with step 0.02° with effective measurement time of 10 s/step. The choice of the scanning interval was based on a quick scan in the first sample in the region of 5–100° in 2θ. The resulting diffractogram was qualitatively interpreted with help of JCPDS-ICDD database comprising information about more than 250, 000 different crystalline compounds. The detection limit is around 0.5 volume-%.

3. Results and discussions

3.1. *Discussion about the digestion procedure*

In order to have a digestion procedure capable of digesting a relatively large number of sample types, a mixture of hydrochloric acid and nitric acid was used consisting of 100 mL concentrated nitric acid (65%), 100 mL concentrated hydrochloric acid (37%), and 60 mL water to 30 g sample. This acid mixture will dissolve many common alloys. In order to make sure metallic parts partly covered with other materials (for instance cables) or relatively large metallic parts were digested, the solution was boiled for an hour. During the relatively long boiling time much of the acids also evaporated making the solution less aggressive when handling it in the next step. Empirically it was found that the amount of acid is sufficient to completely digest 100% of sample containing acid soluble metals. Since the solubility of many salts will be exceeded during digestion, many of the corresponding elements will precipitate as salts already in the digestion step. The resulting mixture was then dried, and then remaining solid material was grinded using a mortar and then dried again. Grinding also resulted in homogenization of some materials that were not digested by the acid mixture such as many silica based materials and polymers. In this way, metals that are not easily grinded are first acid digested prior to grinding. Any large remaining particles have to be isolated and analyzed separately by XRF. The powder was then analyzed as a wax briquette by XRF.

3.2. *Discussion about the XRF measurement procedure*

For the XRF technique the following issues have to be taken into account for a general method analyzing samples with unknown composition: the XRF sample depth, the number of elements, the spectral resolution, the data collection principle, the background estimation, a general calibration, spectral interference corrections for all elements, appropriate mathematical matrix correction, and sample preparation giving samples with suitable homogeneity.

3.2.1. *The XRF sample depth and the number of elements*

Using XRF one can reliably measure the elements of interest in the periodic table except the light elements, e.g. boron, carbon, nitrogen and oxygen. Since only the surface layer is measured with XRF there is a strong demand on homogeneity. For light elements from sodium to silicon where the analyzed layer is relatively thin, only samples that are homogeneous at the sub μm level will give reliable results. The survey analysis procedure proposed here where particles up to 50 μm are accepted will give semiquantitative results for these light elements when such coarse particles are present. With increasing atomic number of the analyte as well as decreasing atomic number of the matrix, the depth of the layer that is analyzed increases and there is less demand on homogeneity.

3.2.2. *Spectral resolution*

For a general analytical procedure for various matrices the selectivity is essential and in XRF the spectral resolution is the key parameter for selectivity. Of the two major XRF measuring principles, wavelength and energy dispersive, both can be used but the energy dispersive has a drawback of lower spectral resolution for most of the elements in lower energy range e.g. Zn interferes with Na determination, as well as in medium energy range e.g. Fe interferes with Co determination. Even if the resolution of wavelength dispersive in general is higher than energy dispersive XRF there are still many interferences that have to be taken into account for a sample of unknown matrix. Therefore instrument set-up has to be optimized not on sensitivity but on spectral resolution by the choice of crystals, collimators, and detector settings. All important interferences have to be assessed for each instrument and instrument set-up.

3.2.3. *Data collection and background estimates*

Of the two data collection principles for wavelength dispersive XRF, scanning or peak measurements, the peak measurement will have lower quantification limits but the background estimate is less robust. The problem of a reliable background correction using the peak measurement principle is addressed by also measuring several separate background positions.

3.2.4. *Calibration, spectral interference correction and matrix correction*

Most XRF vendors today supply their instrument with a general calibration for unknown samples (using terms as standardless, semiquantitative) taking into account major spectral line overlaps and major absorption-enhancement effects due to the sample matrix. With the spectral overlap corrected for the XRF line intensity at a particular wavelength there will still be these absorption and enhancement effects due to main components present in the sample. For homogeneous samples these effects can be accounted for mathematically by the use of fundamental physical influence coefficients for each element present e.g. so called theoretical alfa correction or fundamental parameters [8]. This calibration can be used as a starting point for analysis. Generally the line interference corrections for all major elements possible in the sample have to be checked and if needed adjusted. However the mathematical corrections based on fundamental coefficients will normally not need any adjustments. The prerequisite for a reliable correction for matrix effects is that all elements in the test sample are measured or known, and distributed homogeneously.

The elements validated with this methodology are given in Table 2 where the elements have been divided into three categories and marked as white, light gray, and dark gray. Elements that cannot be determined using XRF, and Cl that cannot be determined with the described method since hydrochloric acid is used in the digestion acid mixture, are marked in dark gray. Elements that are considered not to be relevant to determine (Ar, Kr, Xe, Tc, Po, At, Fr, Ra, and Rf and heavier elements) are marked in light gray. In addition, since lanthanides and actinides are chemically similar to each other, all lanthanides except two and all actinides except one are excluded from the validation study and are also marked in light gray. Hf is chemically similar to Zr and is also excluded. The rest of the elements including two lanthanides (La and Ce) and one actinide (Th) are studied here and are marked in white.

Some elements that can possibly not be digested in the acid solution have been identified in Table 2. However, if these elements are present as relatively small particles (typically less than 50 μm) after grinding quantification will still be possible. Relatively large parts typically consisting of alloys that have not been digested by the acid must be analyzed separately.

For every sample an internal quality control procedure is applied. The alternative lines are checked for consistency. Nearby lines such as $K\alpha$ and $K\beta$ should give similar results. Any discrepancy can be due to interference and a non-correct line overlap correction. Correct line overlap is essential for determining the trace constituents down to the limit of quantification, here set generally to be 0.01%. For element in high concentration ($>10\%$) the overlap corrections for all elements are verified by analyzing high purity elements or compounds. Additionally, a comparison of K and L-lines gives an indication of the homogeneity of the sample. In a matrix where iron is dissolved according to the procedure the critical depth (99%) for Cu $L\beta$ can be calculated using mass absorption coefficients [9] and the geometry of the instruments to be about 4 μm. If similar concentration values in an iron sample are obtained for Cu $K\alpha$ and Cu $L\beta$ lines the prepared sample can be considered homogeneous at a particle size of 4 μm or less based on copper measurements.

3.3. *Characterization of dried powder*

In order to characterize the prepared powder several analyses including determination of metal and elemental chlorine, determination of water soluble chloride and nitrate, and study of crystalline phases by XRD (X-ray diffraction) were performed on powder prepared from three different metals, Al, Cu and Fe, which often are found in high concentrations in many samples, and are expected to react differently from each other in the preparation step. The results of these analyses are summarized in Table 3. In the Al containing powder, Al is mainly present as Cl containing salts with a Cl to Al (Cl/Al) mole ratio of 0.3. Since water soluble chloride only constitutes a minor part (35%) of the total Cl present and since no crystalline phases are present, it is likely that Al is mainly present as amorphous aluminum chlorohydrate salts ($Al_nCl_{3n-m}(OH)_m$). In the Cu containing powder chloride is a main anion with a Cl to Cu (Cl/Cu) mole ratio of 1.4, and XRD data shows that Cu is present as crystalline copper chloride and copper oxychloride. In the Fe containing powder, Fe is present as Cl containing salts with a Cl to iron (Cl/Fe) mole ratio of 0.6. XRD data shows the presence of crystalline iron chloride and iron hydrate phases together with some amorphous material. However, water soluble chloride only constitutes a minor part (15%) of the Cl content which is somewhat contradictory to the XRD results. For all three samples, the nitrate to metal (NO_3^-/metal) mole ratio is <0.08, i.e. nitrate is not a main anion. This is not surprising since nitrate is acting as an oxidant and is consumed in the digestion step. From above it is clear that the non-metal ion part of the powder subsequent to digestion is different from metal to metal but the main element present not measured by XRF is oxygen.

3.4. *Analysis of samples originally containing only elements that can be measured with XRF*

For chemical characterization where over 70 elements are determined the demand on measurement uncertainty is low, and so called standardless programs are fit for purpose. With an XRF instrument calibrated for a standardized sample preparation for a certain type of samples most of the parameters describing the sample and the sample preparation are fixed and do not need to be given in order to evaluate the elemental concentrations in the sample. When using a so called standardless program with universal calibration it is necessary to describe in detail all parameter regarding sample and sample preparation in order to make a reliable evaluation of the elemental concentrations in the sample. The instrument was calibrated with 29 mm collimator and the briquettes are 32 mm so most of the surface area available is measured. Giving the input parameters, sample weight, sample height, and for the briquette preparation the composition of the binder (the wax) and the dilution factor, the elemental concentrations in the sample can be calculated. The elements are specified as elements with a rest (i.e. elements not measured by XRF) consisting only of oxygen. This is a generalization since for metallic samples also nitrogen and some hydrogen are present, and for samples containing polymers carbon will also be present. However, as shown below, assuming oxygen as the only component of the rest will not introduce any major errors in the results.

Table 2
List of elements, original form of the elements in the sample and recovery.

Atomic number	Symbol	Name of element	Comment[a]	Possible insufficient digestion	Original form of element[b]	Sample number	Recovery
1	H	Hydrogen	N.A.	–	–	–	–
2	He	Helium	N.A.	–	–	–	–
3	Li	Lithium	N.A.	–	–	–	–
4	Be	Beryllium	N.A.	–	–	–	–
5	B	Boron	N.A.	–	–	–	–
6	C	Carbon	N.A.	–	–	–	–
7	N	Nitrogen	N.A.	–	–	–	–
8	O	Oxygen	N.A.	–	–	–	–
9	F	Fluorine	N.A.	–	–	–	–
10	Ne	Neon	N.S.	–	–	–	–
11	Na	Sodium	–	–	Salt	3	1.13
12	Mg	Magnesium	–	–	Alloy	1	1.03
13	Al	Aluminum	–	–	Alloy	1, 2	1.11, 0.92
14	Si	Silicon	–	X	Alloy	11	1.06
15	P	Phosphorus	–	–	Salt	3	1.24
16	S	Sulfur	–	–	Salt	3	0.72
17	Cl	Chlorine	N.A.*	–	–	–	–
18	Ar	Argon	N.S.	–	–		–
19	K	Potassium	–	–	Salt	3	0.94
20	Ca	Calcium	–	–	Salt	3	1.11
21	Sc	Scandium	–	–	Solution	8	0.83
22	Ti	Titanium	–	–	Alloy	2	0.86
23	V	Vanadium	–	–	Alloy	2	0.97
24	Cr	Chromium	–	–	Alloy	2	1.00
25	Mn	Manganese	–	–	Alloy	1	1.01
26	Fe	Iron	–	–	Alloy and pure element	1, 3, 4, 6, 11	1.11, 0.98, 1.00, 1.00, 0.84
27	Co	Cobalt	–	–	Alloy	2	0.98
28	Ni	Nickel	–	–	Alloy	1, 2	1.01, 1.01
29	Cu	Copper	–	–	Alloy	1	0.90
30	Zn	Zinc	–	–	Alloy	1	1.01
31	Ga	Gallium	–	–	Solution	8	0.94
32	Ge	Germanium	–	X	Solution	15	0.69
33	As	Arsenic	–	–	Oxide	10	0.98
34	Se	Selenium	–	–	Pure element	10	0.96
35	Br	Bromine	–	–	Salt	5	<0.01
36	Kr	Krypton	N.S.	–			–
37	Rb	Rubidium	–	–	Salt	4	0.90
38	Sr	Strontium	–	–	Salt	4	1.03
39	Y	Yttrium	–	–	Oxide	10	0.92
40	Zr	Zirconium	–	–	Salt	10	1.08
41	Nb	Niobium	–	X	Solution	9	1.08
42	Mo	Molybdenum	–	–	Alloy	2	1.04
43	Tc	Technetium	N.S.	–	–	–	–
44	Ru	Ruthenium	–	X	Solution	14	1.06
45	Rh	Rhodium	–	X	Solution	9, 14	0.97, 0.97
46	Pd	Palladium	–	X	Solution	9, 14	1.10, 1.09
47	Ag	Silver	–	–	Solution	9	1.09
48	Cd	Cadmium	–	–	Pure metal	6	1.07
49	In	Indium	–	–	Solution	8	1.21
50	Sn	Tin	–	–	Alloy	1	0.96
51	Sb	Antimony	–	–	Pure metal	6	1.03
52	Te	Tellurium	–	–	Solution	8	1.39
53	I	Iodine	–	–	Salt	5	<0.01
54	Xe	Xenon	N.S.	–			–
55	Cs	Cesium	–	–	Salt	4	1.02
56	Ba	Barium	–	–	Salt	4	0.98
57	La	Lanthanum	–	–	Alloy	6	1.04
58	Ce	Cerium	–	–	Alloy	6	0.94
59	Pr	Praseodymium	N.S.	–	–	–	–
60	Nd	Neodymium	N.S.	–	–	–	–
61	Pm	Promethium	N.S.	–	–	–	–
62	Sm	Samarium	N.S.	–	–	–	–
63	Eu	Europium	N.S.	–	–	–	–
64	Gd	Gadolinium	N.S.	–	–	–	–
65	Tb	Terbium	N.S.	–	–	–	–
66	Dy	Dysprosium	N.S.	–	–	–	–
67	Ho	Holmium	N.S.	–	–	–	–
68	Er	Erbium	N.S.	–	–	–	–
69	Tm	Thulium	N.S.	–	–	–	–
70	Yb	Ytterbium	N.S.	–	–	–	–
71	Lu	Lutetium	N.S.	–	–	–	–
72	Hf	Hafnium	N.S.	–	–	–	–
73	Ta	Tantalum	–	X	Solution	9	1.07
74	W	Tungsten	–	X	Solution	9	1.01

Table 2 (*continued*)

Atomic number	Symbol	Name of element	Comment[a]	Possible insufficient digestion	Original form of element[b]	Sample number	Recovery
75	Re	Rhenium	–	X	Solution	14	0.78
76	Os	Osmium	–	X	Solution	14	< 0.5
77	Ir	Iridium	–	X	Solution	9, 14	0.94, 0.97
78	Pt	Platinum	–	X	Solution	9, 14	0.92, 1.00
79	Au	Gold	–	–	Pure metal and solution	12, 14	0.98, 0.97
80	Hg	Mercury	–	X	Solution	7	< 0.5
81	Tl	Thallium	–	–	Salt	4	1.05
82	Pb	Lead	–	–	Alloy	1	0.85
83	Bi	Bismuth	–	–	Pure metal	6	1.01
84	Po	Polonium	N.S.	–	–	–	–
85	At	Astatine	N.S.	–	–	–	–
86	Rn	Radon	N.S.	–	–	–	–
87	Fr	Francium	N.S.	–	–	–	–
88	Ra	Radium	N.S.	–	–	–	–
89	Ac	Actinium	N.S.	–	–	–	–
90	Th	Thorium	–	–	Solution	13	1.45
91	Pa	Protactinium	N.S.	–	–	–	–
92	U	Uranium	N.S.	–	–	–	–
93	Np	Neptunium	N.S.	–	–	–	–
94	Pu	Plutonium	N.S.	–	–	–	–
95	Am	Americium	N.S.	–	–	–	–
96	Cm	Curium	N.S.	–	–	–	–
97	Bk	Berkelium	N.S.	–	–	–	–
98	Cf	Californium	N.S.	–	–	–	–
99	Es	Einsteinium	N.S.	–	–	–	–
100	Fm	Fermium	N.S.	–	–	–	–
101	Md	Mendelevium	N.S.	–	–	–	–
102	No	Nobelium	N.S.	–	–	–	–
103	Lr	Lawrencium	N.S.	–	–	–	–
104	Rf	Rutherfordium	N.S.	–	–	–	–
105	Db	Dubnium	N.S.	–	–	–	–
106	Sg	Seaborgium	N.S.	–	–	–	–
107	Bh	Bohrium	N.S.	–	–	–	–
108	Hs	Hassium	N.S.	–	–	–	–
109	Mt	Meitnerium	N.S.	–	–	–	–
110	Ds	Darmstadtium	N.S.	–	–	–	–
111	Rg	Roentgenium	N.S.	–	–	–	–
112	Cn	Copernicium	N.S.	–	–	–	–
113	Uut	Ununtrium	N.S.	–	–	–	–
114	Uuq	Ununquadium	N.S.	–	–	–	–
115	Uup	Ununpentium	N.S.	–	–	–	–
116	Uuh	Ununhexium	N.S.	–	–	–	–
117	Uus	Ununseptium	N.S.	–	–	–	–
118	Uuo	Ununoctium	N.S.	–	–	–	–

[a] N.A.=not applicable, N.A.*=not applicable since hydrochloric acid is used for digesting the samples, N.S.=not studied.

[b] See Table 4.

Since Cl and light elements not measured by XRF such as H, N, and O are incorporated into the analyzed material in the sample preparation step, the concentration of the individual elements, x, in the original sample in mass-%, c_x, will be obtained from

$$c_x = \frac{c_{x,XRF}}{\left(\sum_n c_{n,XRF}\right) - c_{Cl,XRF}} \times 100\% \qquad (1)$$

where $c_{x,XRF}$ and $c_{Cl,XRF}$ are the concentration of individual elements and Cl, respectively, in the measurement matrix determined by XRF.

3.5. *Analysis of reference materials*

In order to evaluate the analytical procedure different samples were prepared in the laboratory. The source of the elements (alloy, pure metal or element, oxide, salt, or solution) is given in Table 2, and the composition of the prepared samples is given in Table 4. Alloys were used as source for most elements. Alkali metals and alkaline earth metals except Mg were added as salts, and some relatively unusual elements were added as compounds (salts or oxides) or as solutions. In addition, elements that are not readily digested by the nitric acid and hydrochloric acid mixture, including Nb, Ru, Rh, Pd, Ag, Te, Ta, W, Os, Ir, Pt, and Hg were added as solutions. Typically 6 g of the prepared samples were acid digested. After analysis of the samples, the recoveries for the different elements were calculated.

Recoveries for the elements are given in Table 2, and shown as a function of atomic number and assigned concentrations in Fig. 1(a) and (b), respectively. All elements except six had recoveries higher than 0.8. The six elements with recoveries lower than 0.8 included S, Ge, Br, I, Os and Hg and the loss of these elements is further discussed below. Two elements, Te and Th, had relatively high recoveries of 1.39 and 1.45, respectively, and this is likely due to a calibration deficiency. There is no correlation between recovery and atomic number as can be seen from Fig. 1(a). The recoveries are more scattered at lower assigned concentrations (see Fig. 1(b)) which is expected.

3.6. *Loss of elements due to volatility*

Some elements, including As, Br, Cr, Ge, Hg, I, Os, Re, Ru, Sb, S, Se, and Sn, can form volatile compounds and hence there is a risk that these elements will be lost during the sample preparation steps [10]. Hg can evaporate as metallic Hg or possibly as chloride [10], Os and Ru can evaporate as tetroxides [10], As, Ge, Re, Sb, Se,

Table 3
Content of metal, water soluble nitrogen–nitrate (N–NO_3) and chloride (Cl^-), elemental chlorine (Cl), and XRD study of crystalline phases in powder prepared from samples of pure aluminum (Al), pure copper (Cu), and pure iron (Fe).

Sample	Concentration of metal (mass-%)	Water soluble N-NO_3^- (mass-%)	Water soluble Cl^- (mass-%)	Cl (mass-%)	XRD study of crystalline phases
Pure Al	25	1.0	3.2	9	No clear evaluation of crystalline phases. Major part amorphous material.
Pure Cu	46	0.69	36	36	Crystalline copper chloride and copper oxychlorides phases. Little amorphous material.
Pure Fe	49	<0.02	2.8	17	Crystalline iron chloride and iron hydrate phases. Some amorphous material.

Table 4
Composition of prepared samples.

Sample	Sample composition and amount of elements	Elements
1	3.00 g BCS 181/3, 3.00 g IPT Amostra Padro 10A	Mg, Al, Mn, Fe, Ni, Cu, Zn, Sn, Pb
2	3.00 g BCS/SS 310/1, 3.00 g BCS/SS no 345	Al, Ti, Cr, Co, Ni, V, Mo
3	0.600 g NaCl, 0.600 g KCl, 0.600 g KH_2PO_4, 0.600 g Na_2SO_4, 0.600 g $CaCl_2$ $2H_2O$, 3.00 g Fe	Na, K, P, S, Ca, Fe
4	0.600 g CsCl, 0.600 g $BaCO_3$, 0.600 g $Sr(NO_3)_2$, 0.120 g RbCl, 0.120 g $TlNO_3$, 3.96 g Fe	Cs, Ba, Sr, Rb, Tl, Fe
5	1.50 g NaBr, 1.50 g NaI, 3.00 g Fe	Na, Br, I, Fe
6	1.92 g Fire Steel, 1.00 g Bi, 1.00 g Sb, 0.300 g Cd, 1.78 g Fe	Ce, La, Bi, Sb, Cd, Fe
7	5.98 g Fe, 15.0 mL 1000 mg L^{-1} Hg	Fe, Hg
8	5.91 g Fe, 30.0 mL 1000 mg L^{-1} Te and Sc, 15.0 mL 1000 mg L^{-1} In and Ga	Fe, Te, Sc, In, Ga
9	5.85 g Fe, 30.0 mL 1000 mg L^{-1} W, Nb, Pt and Ag, 15.0 mL 1000 mg L^{-1} Rh, Ta, Ir and Pd	Fe, W, Nb, Pt, Ag, Rh, Ta, Ir, Pd
10	5.10 g Fe, 0.100 g Se, 0.200 g As_2O_3, 0.300 g $YCl_3 \cdot 6H_2O$, 0.300 g $ZrOCl_2 \cdot 8H_2O$	Fe, Se, As, Y, Zr
11	6.00 g FeSi alloy	Fe, Si
12	5.48 g Fe, 0.520 g Au	Fe, Au
13	5.98 g Fe, 15.0 mL 1000 mg L^{-1} Th	Fe, Th
14	5.88 g Fe, 150 mL 100 mg L^{-1} Au, Ir, Os, Pd, Pt, Re, Rh and Ru	Fe, Au, Ir, Os, Pd, Pt, Re, Rh, Ru
15	5.95 g Fe, 50 ml 1000 mg L^{-1} Ge	Fe, Ge

and Sn can evaporate as chlorides [10], Cr can evaporate as chromyl chloride, S can evaporate in several different forms, and Br and I can evaporate as acids.

Of the potentially volatile elements, Br (present originally as bromide), I (present originally as iodide), Hg (present originally as mercury(II)) and Os were completely lost (see Table 2). The elements As, Cr, Re, Ru, Sb, Se, Sn had recoveries in the range 0.8–1.1, and were considered to be not lost. S (originally present as sulfate) and Ge had recoveries of 0.7 and were considered to be partly lost. S can however be present in several other forms that are relatively volatile and determination of S is not a straightforward task and needs to be studied in detail.

Some other elements might also be lost in the special case of samples containing relatively high concentrations of fluoride since some elements can form volatile fluoride compounds including As, Ge, Nb, Sb, Se, Si, Ta, Te, and Ti [10].

3.7. Analysis of samples containing undigested inorganic materials

Many silicon containing materials, minerals, metals, and alloys will not be digested in acid mixtures of nitric acid and hydrochloric acid. However, silicon based materials and minerals can most often be grinded to sufficiently small particles. Metals and alloys can generally not be grinded, and parts containing metals or alloys that are not digested by the acid mixture must be removed and analyzed separately. Hence, presence of undigested metals and alloys should most often not be a problem.

3.8. Analysis of samples originally containing light elements and volatile compounds using internal standard

When calculating concentrations of individual elements with Eq. (1), Cl and light elements such as H, N, and O that are incorporated into the sample matrix during the sample preparation step, are excluded. However, if the sample originally contains Cl and light elements not measured by XRF (such as H, C, N, and O), an internal standard can be introduced in order to be able to obtain concentration of elements in the original sample. The concentration of individual elements in the original sample, $c_{x,sample}$, will then be calculated from

$$c_{x,sample} = \frac{c_{x,IS,XRF}}{c_{IS,XRF}} \times \frac{m_{IS}}{m_{sample}} \times 100\% \qquad (2)$$

where $c_{x,IS,XRF}$ and $c_{IS,XRF}$ are the concentration of the individual elements and the internal standard, respectively, in the measurement matrix determined by XRF in the presence of an internal standard in the sample, m_{IS} is the mass of added internal standard, and m_{sample} is the mass of the original sample (not including the internal standard).

In order to investigate how well an internal standard compensates for the presence of organic material, samples consisting of 6 g of 50.0% poly(methyl methacrylate) (PMMA), 25.0% Cu-Al-alloy (BCS 181/3), and 25.0% bronze (IPT Amostra Padro 10A) were prepared and analyzed without and with 0.414 g Sr as internal standard added as 1.00 g strontium nitrate. Sr was chosen as an internal standard since the original concentration of Sr in most samples generally is low and negligible compared to the concentration used here, Sr has a recovery close to 1 (see Table 2), and the line energy of the Sr Kα line is 14.14 keV and located in the middle of the measured line energy range. The results are given in Table 5 where recoveries without and with internal standard are given for the different elements, their atomic number, and their assigned concentrations. The relationship between recovery and atomic number and line energy of the elements without and with internal standard is shown in Fig. 2(a) and (b), respectively. Without use of an internal standard, the presence of 50% PMMA results in recoveries around 2 to 3 for elements with atomic number above 20 that are measured at line energies above 5 keV since presence of PMMA is not considered in the evaluation. The lightest elements Al and Mg measured at

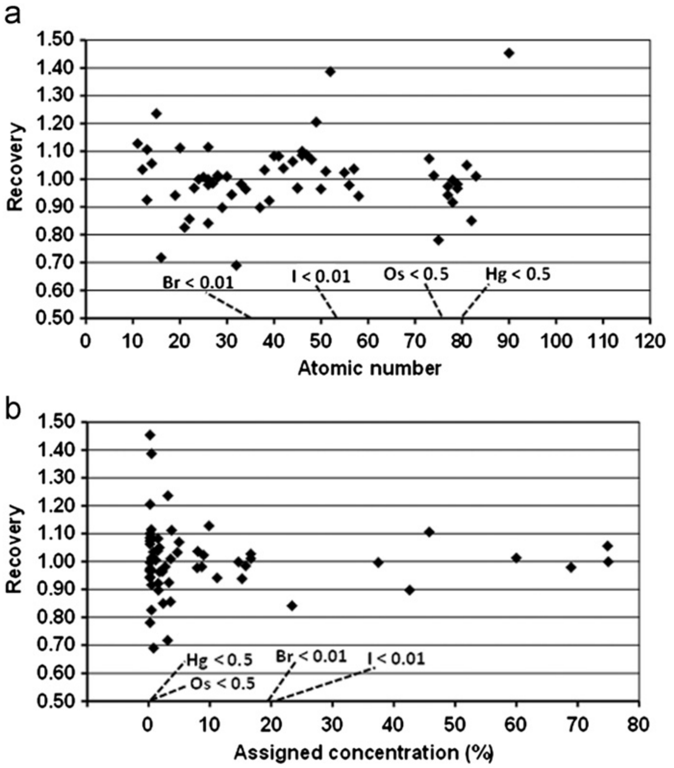

Fig. 1. Recoveries for elements as a function of (a) atomic number and (b) assigned concentration. Br and I had recoveries <0.01, and Os and Hg had recoveries <0.5, and these elements have been marked specifically in the figures.

Table 5
Results from analysis of a 6.00 g sample consisting of a mixture of 50% PMMA, 25% Cu–Al–alloy, and 25% bronze, without and with 0.414 g Sr (added as 1.00 g strontium nitrate) as internal standard.

Element	Atomic number	Assigned concentration (%)	Recovery without internal standard	Recovery with internal standard
Mg	12	0.39	1.46	0.85
Al	13	23	1.84	0.96
Mn	25	0.28	2.12	1.11
Fe	26	0.23	2.71	1.31
Ni	28	0.58	2.23	1.15
Cu	29	21	2.15	1.07
Zn	30	1.8	2.19	1.11
Sn	50	1.1	2.32	1.14
Pb	82	1.2	1.96	0.95

relatively low line energies below 5 keV have recoveries around 1.5 since the signal of these elements is attenuated more than the other elements by the presence of light elements. When Sr (atomic number 38, measured using the Kα line at 14.14 keV) is used as an internal standard, recoveries of all the elements measured are in the range 0.85–1.15, except Fe that has a relatively high recovery of 1.31. Hence, an internal standard can be utilized to compensate for the presence of for instance organic materials, e.g. different polymers, or chlorine containing material.

Although the non-measurable elements are not directly quantified, the summarized concentration of the elements not determined by XRF originally present in the sample can be obtained as the undetermined rest of the sample. For the studied sample that originally consisted of 50.0% PMMA, an undetermined rest of 49.2% was obtained.

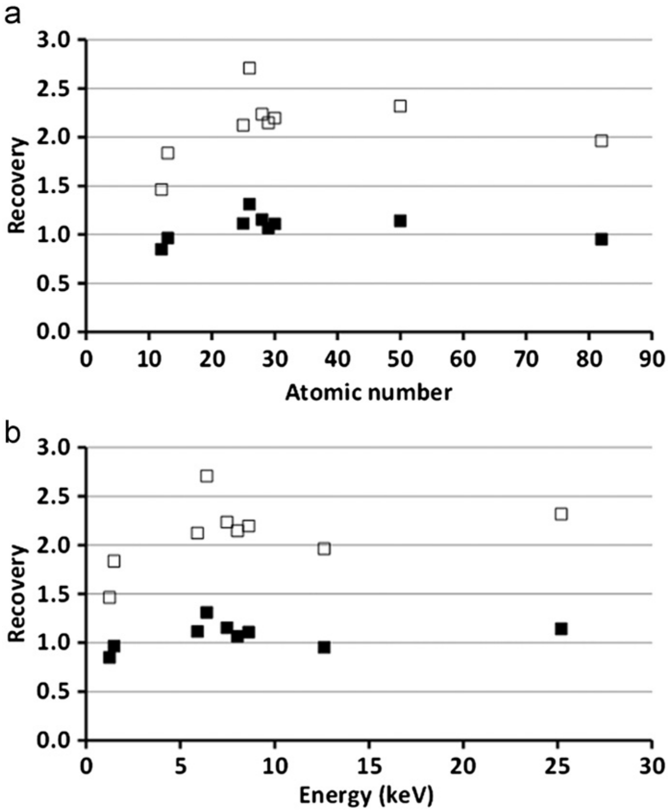

Fig. 2. Recoveries as a function of (a) atomic number and (b) energy for elements when analyzing 6.00 g sample consisting of 50% PMMA, 25% Cu-Al-alloy, and 25% bronze (☐) without and (■) with 0.414 g Sr (added as 1.00 g strontium nitrate) as internal standard.

The results also demonstrates that O can be used to describe the rest in the sample matrix not measured by XRF in the evaluation although other elements such as H, C, and N are present as major components in the rest.

Although not demonstrated, the use of an internal standard will also compensate for the weight loss of elements during the sample preparation step due to the presence of volatile compounds in the sample such as water and volatile organic compounds.

4. Conclusions

Elemental survey analysis of inhomogeneous and unknown samples such as waste is associated with relatively large difficulties including high degree of inhomogeneity, presence of many different materials and compounds that are not known and that have different chemical properties, possibility that the elements are present in different forms (e.g. elemental, or as oxides or salts, or incorporated into a plastic matrix), and a demand to measure most (preferably all) of the elements in the periodic table. The described work is a strategy that addresses these difficulties.

Fig. 3 shows the periodic table of the elements, and the elements that can be determined by the described procedure are marked in dark gray. Only two lanthanides (La and Ce) and one actinide (Th) have been studied; however since all lanthanides and actinides are chemically similar it is likely that all these compounds can be determined. Hence, lanthanides and actinides not studied have also been marked. Also Hf is marked since it is chemically similar to Zr. S and Ge are marked in light gray since they can be partly lost.

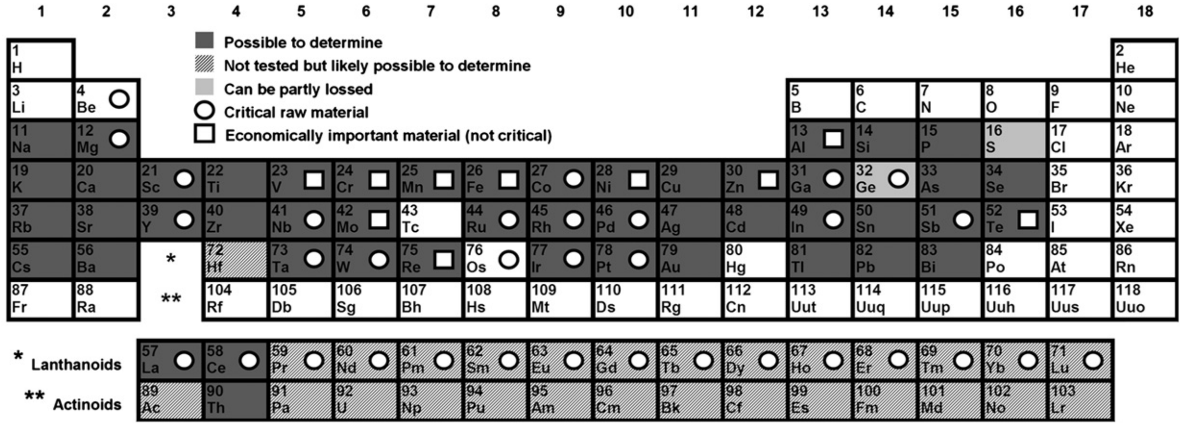

Fig. 3. Periodic table showing the elements that are possible to determine with the described technique. (○) Elements that are considered to be critical raw material and (□) elements that are considered to be of economic importance but not critical.

As discussed above, some limitations of the sample preparation and analysis procedure exist and have been identified including lack of possibility to determine light elements (including H to F) by XRF, loss of some elements by volatilization (S, Ge, Br, I, Os, and Hg), and insufficient digestion of some elements and materials in the acid mixture. However, by using an internal standard, the influence of light elements and chlorine on the evaluation of other elements can be reduced. Although volatilization is normally limited to 6 elements, in the special case of samples containing relatively high concentrations of fluoride, some elements can form volatile fluoride compounds. Insufficient digestion is possible for many materials; however, only materials that can neither be grinded nor acid digested will be a problem. Parts consisting of such materials must be removed and analyzed separately.

Recently, within the framework of the EU Raw Materials Initiative several raw materials have been classified as critical raw materials based on their high relative economic importance and high relative supply risk [1,3]. In addition, several additional raw materials have high relative economic importance but are not classified as critical raw material due to a relatively low supply risk [1,3]. Most of these materials are elements and these have been marked in Fig. 3. In order to secure access to these materials, recycling will be of major importance in the future. In order to improve the efficiency of recycling, survey analysis of waste fractions from different sources is needed. Some of the elements considered as critical or as only of economic importance including e.g. the platinum group metals and the rare earths elements are generally present in waste at concentrations below approximately 0.002% which can be difficult to detect by XRF. However, by using other techniques such as ICP-MS sufficiently low detection limits will be obtained also for these elements. In addition, determination of Be will be possible. The combination of the described homogenization step with ICP-MS will be explored in the future.

Acknowledgment

Dr. Vratislav Langer at Chalmers University of Technology (Göteborg, Sweden) is acknowledged for performing the XRD analysis.

References

[1] Critical Raw Materials for the EU, Report of the Ad-hoc Working Group on defining critical raw materials, 2010. Available at 〈http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/report-b_en.pdf〉, last accessed at 2011-11-10.
[2] H.-Y. Kang, J.M. Schoenung, Resour. Conserv. Recycling 45 (2005) 368–400.
[3] Annex V, Critical Raw Materials for the EU, Report of the Ad-hoc Working Group on defining critical raw materials, 2010. Available at 〈http://ec.europa.eu/enterprise/policies/raw-materials/files/docs/annex-v-b_en.pdf〉, last accessed at 2011-11-10.
[4] P. Bode, in: R.A. Meyers (Ed.), Encyclopedia of analytical chemistry, John Wiley & Sons Ltd, Chichester, UK, 2008, p. 1.
[5] F. Claisse, in: Z. Mester, R. Sturgeon (Eds.), Sample preparation for trace element analysis, Elsevier, Amsterdam, The Netherlands, 2003, p. 301.
[6] G.O.H. Bennet, XRF analysis of ceramics, minerals and allied materials, John Wiley & Sons Ltd, Chichester, England, 1992.
[7] M.H. Ramsey, S.L.R. Ellison, EURACHEM/ CITAC Guide Measurement uncertainty arising from sampling—a guide to methods and approaches, 2007. Available from the Eurachem secretariate.
[8] R.M. Rousseau, Spectrochim. Acta Part B: At. Spectroscopy 61 (2006) 759–777.
[9] J.H. Hubbel, S.M. Seltzer, Tables of X-ray mass attenuation coefficients and mass energy-absorption coefficients from 1 keV to 20 MeV for Elements $Z=1$ to 92 and 48 Additional Substances of Dosimetric Interest, 1996. Available at 〈http://www.nist.gov/pml/data/xraycoef/index.cfm〉, last accessed at 2012-02-08.
[10] R. Book, Handbook of Decomposition Methods in Analytical Chemistry, International Textbook Company Ltd., The Blackie Group, Glasgow, New Zeeland, 1979.