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A Partially Mechanized System for the Combustion of Organic Samples in a Stream of Oxygen with Quantitative Recovery of the Trace Elements

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Teilmechanisiertes System zur Verbrennung organischer Proben im Sauerstoffstrom mit quantitativer Wiedergewinnung der Spurenelemente

Zusammenfassung. Ein teilmechanisiertes aus Quarz bestehendes System (Trace-0-Mat) wird beschrieben, das die vollständige Mineralisation fester organischer oder biologischer Proben bis zu Mengen von 1 g gestattet. Die Verbrennung findet dabei in reinem Sauerstoff in einer sehr kleinen Verbrennungskammer (etwa 75 cm^3) statt, so daß anschließend die metallischen und nichtmetallischen Spurenelemente mit hoher Zuverlässigkeit bestimmt werden können. Die steuerbare Veraschung wird durch ein System von IR-Strahlern gestartet. Alle flüchtigen Spurenelemente (z.B. Hg, Se, Te, As, Sb, I) werden zusammen mit den Verbrennungsprodukten in einem Kühlsystem kondensiert, das mit flüssigem Stickstoff gefüllt und über der Verbrennungskammer angeordnet ist. Die sich an den gekühlten Flächen befindlichen flüchtigen sowie die in der Asche vorhandenen nichtflüchtigen Elemente werden durch Rückflußbehandlung mit einer kleinen Säuremenge (2 ml) gelöst und in einem Quarzglas unterhalb der Verbrennungskammer gesammelt.

Die Wiederfindung der Elemente nach dem Aufschlußprozeß (50–60 min) wurde mit Hilfe von 7 NBS-Referenzmaterialien für folgende Elemente geprüft: B, Cr, Cu, Fe, Mn, Zn (ICP-Emissionsspektrometrie), Cd, Pb (ETA-AAS), Hg (AAS-Kaltdampftechnik), As (AAS-Hydridmethode) und Se (Röntgenfluorescenz). Es ergab sich sehr gute Übereinstimmung mit den zertifizierten Werten. Diese neue und sehr allgemein anwendbare Aufschlußmethode weist nicht nur geringe Blindwerte auf, sondern vermeidet auch wesentliche Verluste der zu bestimmenden Elemente durch Verflüchtigung, Adsorption oder Zusammenbacken an der Quarzoberfläche. Durch die einfache Handhabung der Apparatur ist eine zuverlässige Bestimmung von Spurenelementen im µg/g- und ng/g-Bereich für die meisten nichtflüchtigen organischen Matrices gewährleistet.

Summary. A partially mechanized apparatus made of quartz (Trace-0-Mat) is described that permits the complete mineralization of up to 1 g of organic or biological solid samples. The combustion takes place in pure oxygen in a very small burning chamber (ca. 75 cm^3) to subsequently determine metallic and non-metallic trace elements (1 ng/g) with high reliability. The controllable incineration is started with an IR-radiator system. All volatile trace elements (e.g. Hg, Se, Te, As, Sb, I) are condensed together with the products of the combustion process in a cooling system filled with liquid nitrogen that is mounted on top of the burning chamber. Subsequent refluxing with a suitable acid in a quartz test tube mounted below the burning chamber collects both the volatilized elements from the

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cooled areas and nonvolatile elements in the ashing residue. The volume of the acid is about 2 ml.

The recoveries of the elements following the decomposition process that takes 50 – 60 min for one sample was checked using 7 NBS-Standard Reference Materials for the elements B, Cr, Cu, Fe, Mn, Zn (ICP-emission spectrometry), Cd, Pb (ETA-AAS), Hg (AAS-cold vapor technique), As (AAS-hydride method) and Se (XRF). Very good agreement with the certified values was observed. This furnished evidence that this new and very general decomposition method is not only poor in blanks but also avoids substantially losses of the elements to be determined by volatilization, adsorption or even baking in the quartz surface. The easy handling of the apparatus offers the best premises for a reliable determination of trace elements in the µg/g and ng/g range in most non-volatile organic matrices.

Key words: Best. von Elementspuren in Organ. Material; Verbrennungsapparatur; Sauerstoffstrom

Introduction

The decomposition of samples is an important operation in a multi-stage combined procedure for the determination of inorganic trace constituents in organic matrices. In spite of the large number of decomposition methods [1] there is still a need for an universal technique – largely free of blanks and systematic errors –, that satisfies the reliability requirements of the extreme trace analysis of elements [9]. By far the most favourable conditions exist by combustion of the organic sample in pure oxygen. But even modifications of this technique [1] are very unsatisfactory for the application in extreme trace analysis because losses of elements by volatilization, adsorption or even baking in the surface of the vessel can occur and can lead to systematic errors difficult to recognize.

In the oxygen flask combustion introduced by Hempel and further developed by Schöniger [6] elemental loss by volatilization is avoided. Samples of 10 – 50 mg weight are burned in a closed oxygen-filled flask with a volume of 250 – 500 ml. Even though this is a very powerful method for micro elemental analysis, it cannot be applied to trace analysis without serious drawbacks: either the initial sample weight is too small or – with larger sample weights – the ratio of vessel surface to sample is unfavourable since large volumes have to be employed. An incineration of large amounts of sample in a closed system under pressure [5] also leads to systematic errors because of the considerable size of the vessel and in ultra-trace analysis because of contamination caused by the material (stainless steel). However, for routine determinations of higher contents of traces (µg/g-range) the experience gained with this method is satisfactory.

The incineration of larger samples for the determination of trace elements at ng/g levels can only be accomplished by continuously supplying oxygen using a small vessel made of inert material. To attain a closed leak-free system in spite of the aforementioned need for continuous oxygen supply, the gaseous products of the combustion process have to be condensed with liquid nitrogen [3, 8]. The volume of the burning chamber made of quartz is only about 75 cm^3 in this "quasi-static" system and allows to use sample weights up to 1 g. In the upper part of the quartz apparatus which is constructed as a cooling finger and cooling jacket all volatile trace elements are condensed, as are the combustion products, CO_2 and H_2O. Afterwards the elements which find themselves in part on the cooling areas and in the ash are dissolved by refluxing with a minimal amount of acid and collected in a test tube located at the lower end of the apparatus.

In the current paper this principle was used to develop a powerful partially mechanized decomposition method for the reliable determination of metallic and non-metallic trace elements in the µg/g and ng/g range in non-volatile organic matrices.

1. Description of the Method

1.1. Decomposition Apparatus

The partially mechanized combustion apparatus (Trace-0-Mat)[1] (Fig. 1) consists of a combustion unit made of quartz and the accessories necessary for the mechanized operation. All components are assembled in a stainless steel box. The combustion unit is located behind a safety door made of coloured plexiglass.

1.1.1. Combustion Unit. The all-quartz combustion unit (Fig. 2) is divided into three zones according to its functions: the burning chamber (*I*), over the cooling unit (*II*) and beneath a test tube with the sample holder (*III*).

The burning chamber (*I*) is cylindrical (40 mm i.d., 60 mm height). At its lower side is a grounded connection for the test tube (*III*) in which a sample holder made of quartz is positioned so that the sample can be introduced into the burning chamber from below. The length of the sample holder is such that the sample reaches the lower third of the burning chamber. The feed of oxygen is accomplished through a water cooled capillary, the functioning of which is described in Chap. 2.1. The oxygen is introduced tangentially into the burning chamber (sectional view A-A, Fig. 2).

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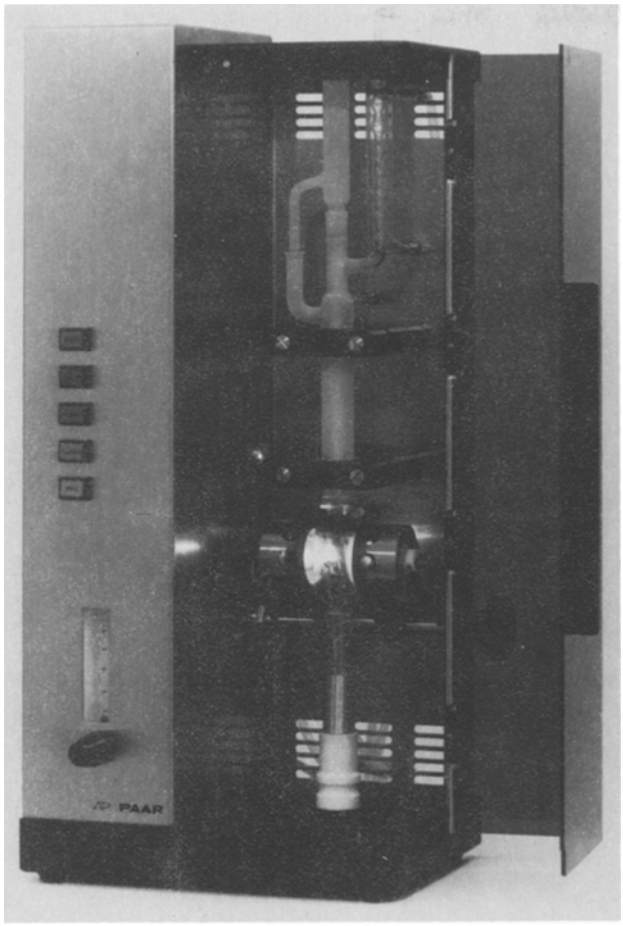

Fig. 1. Decomposition apparatus

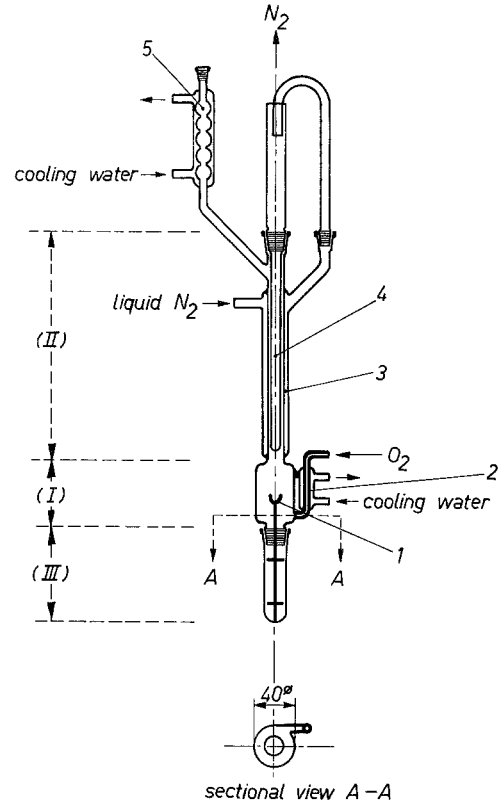

Fig. 2. Combustion unit. (*I*) Burning chamber; (*II*) Cooling unit; (*III*) Ground test tube. *1* Sample holder; *2* Capillary (O_2-inlet); *3* Cooling jacket; *4* Cooling finger; *5* Water cooled condenser

The cooling unit (*II*) on top of the burning chamber (*I*) is positioned. It consists of a cooling jacket and a cooling finger which are filled with liquid nitrogen prior to the incineration. On top of it, another condenser with water is located.

1.1.2. Control Unit. All electrical and mechanical parts necessary for an undisturbed execution of the combustion process are defined to constitute the "control unit".

Liquid nitrogen is pumped by a membrane pump from a Dewar vessel into the cooling system of the combustion unit. This pump produces an oscillating air column that is fed into a quartz valve by a silicone hose. This valve dips into the Dewar filled with liquid nitrogen and delivers the coolant into the cooler by a second silicone hose (Fig. 3).

The ignition of the organic sample and the boiling of the acid in the test tube is accomplished with two infrared radiators (Fig. 4). For the ignition both radiators are brought into the upper position (burning chamber), for boiling the acid, into the lower position (test tube). The optimal radiator power and duration of the incineration process is guaranteed by the electronic control. The control unit also takes over the opening of the oxygen valve at the beginning of the incineration process, as well as its closing at the beginning of the refluxing. The oxygen flow is finely regulated by a needle valve and can be read from a flow meter. For an uniform boiling of the acid the

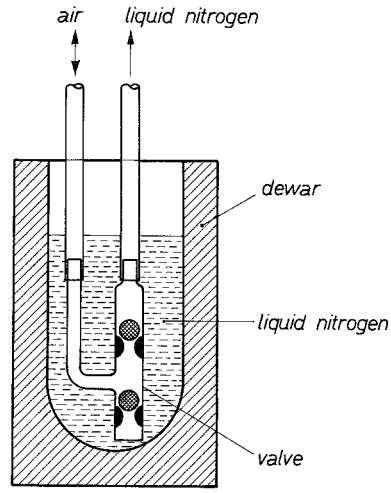

Fig. 3. Dewar vessel with liquid nitrogen and valve of the nitrogen pump

test tube is surrounded by a metal cartridge that is heated by the IR-radiators.

1.2. Reagents

Nitric acid "suprapur" quality (65%); chloric acid/perchloric acid (20/7%), order 10741, E. Merck, Darmstadt; acetone p.a., hydrochloric acid "suprapur" quality, E. Merck, Darmstadt. Water double distilled in a quartz apparatus.

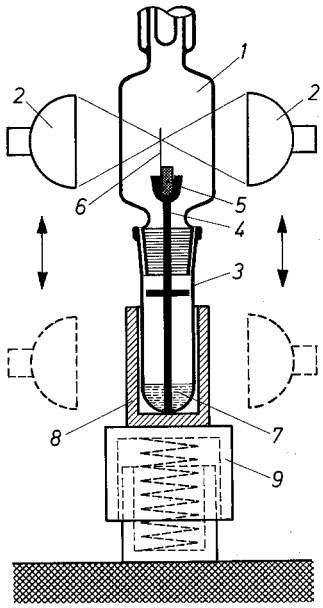

Fig. 4. Ignition and boiling device. *1* Burning chamber; *2* IR-radiators; *3* Test tube; *4* Sample holder; *5* Sample as a pressed pellet; *6* Match cord made of filter paper; *7* Acid; *8* Metal cartridge; *9* Spring construction

1.3. Execution of the Combustion

The working cycle of one incineration can be subdivided as follows: sample preparation – positioning of the sample in the burning chamber – filling of the cooling unit with liquid nitrogen – ignition and combustion of the sample – thawing the combustion products – accumulation of the released elements by refluxing the acid – rinsing and drying of the combustion unit.

Up to 0.5 g of the sample (for some matrices as much as 1 g of the sample can be taken) is pressed to a pellet 7 mm in diameter, or alternatively if pressing is not possible, the sample is wrapped in an ashfree filter paper. For pelleting a small manual press[2] can be used; it is equipped with a press head made of hardmetal to avoid a contamination of the sample. The pellet or the wrapped-in sample is put on the sample holder. A match cord of ashfree filter paper (2 cm long, 4 mm wide) is stuck between the sample and the sample holder. The length of the sample holder is such that only the match cord but not the sample is positioned in the focus of the IR-lamps. This avoids an explosion like incineration of the sample that is experienced if the sample is irradiated directly.

The sample holder is put into the test tube, which is put into the metal cartridge and pressed from below onto the burning chamber with a spring.

Liquid nitrogen is pumped into the cooling unit until cooling mantle and finger are filled. During the incineration the pump is operated periodically to make up for the evaporated liquid nitrogen.

To ignite the sample the IR-radiators are put into the upper position. A safety switch prevents the ignition before the safety door is closed. After pushing the ignition-button the IR-radiators are burning for 30 s with full power. At the same time the magnetic valve for the oxygen is opened. In most cases an O_2-stream of 80–100 l/h will give good results. The incineration lasts, depending on the sample size and the matrix, up to several minutes. Especially for large sample sizes it can be observed that the oxygen flow decreases as the incineration proceeds. The reason for this is that the cooling unit is progressively clogged with combustion products. The sample size must not be so large that the cooling unit is choked completely.

After the combustion the test tube and the burning chamber are disconnected. The sample holder is turned upside down using a pair of tweezers, so that the part used for holding the sample during the combustion is now positioned at the bottom of the test tube. The test tube is filled with 2 ml of acid (in most cases nitric acid) and together with the metal cartridge put back onto the burning chamber.

To collect the elements that are released during the incineration the acid is boiled under reflux using the IR-radiators after having turned them into the lower position. The cooling unit needs to thaw before the acid is heated to boil. This can either be done with a hand fan or, in later development stages of the apparatus, automatically by a built-in fan. After starting the boiling procedure the fan is turned on for 5 min and afterwards the IR-lamps are run at reduced power for about 30 min. The oxygen supply is interrupted during this operation. The acid fumes condense in the water filled condenser and flow back through the entire apparatus into the test tube to dissolve the trace elements and combustion residue from the quartz surface.

After boiling under reflux the apparatus is left to stand for 15–20 min to cool down. Only then the test tube may be taken off. Before starting a new incineration cycle the apparatus must be rinsed and dried. To do this, a beaker is put beneath the burning chamber. First water and then acetone is squirted through the apparatus. After rinsing the burning chamber is closed with a test tube and the oxygen supply is turned on for 2 min. After this procedure the apparatus is dry and ready for the next combustion.

2. Optimization of Parameters

2.1. Oxygen Delivery

The way in which oxygen is delivered into the burning chamber is important for a complete and uniform combustion. Studies concerning the dependence of the combustion from the inlet angle showed that the sample burns slower and more uniform if the oxygen is delivered tangentially. Additionally, in the outer part of the burning chamber the oxygen supply is highest, so that a condensation of unburned sample on surface of the burning chamber is avoided. The intensity of the oxygen stream hardly affects the combustion speed if it is supplied tangentially. An oxygen mass stream between 80 and 100 l/h can be used for nearly all types of samples.

During the refluxing acid fumes diffuse into the oxygen supply line. To prevent a deep penetration, the oxygen supply line is formed like a watercooled capillary. The fumes condense at this spot and shut the supply line.

A small stream of oxygen during refluxing would also prevent penetration. However, losses of volatile trace elements were observed.

2.2. Sample Holder

Geometry and material of the sample holder can be responsible for element losses during the incineration.

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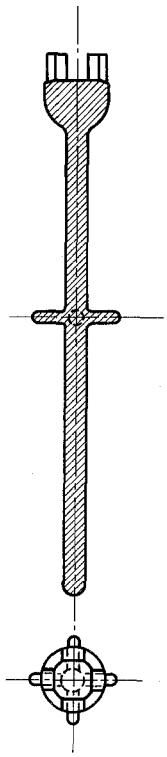

Fig. 5. Sample holder

The elements released by the incineration diffuse to a varying extent into the surface of the sample holder and cannot be redissolved by boiling in nitric acid.

Sample holders made of quartz, platinum, tantalum and titanium have been investigated. Between 5 and 30 % of the elements are irreversibly bound by these materials, whereas the losses could be lowered to 3 % by using a water-cooled sample holder made of quartz. In practical operation the handling of the water-cooled sample holder is cumbersome. The heat can be removed adequately from the burning zone by an appropriate shape of the sample holder (Fig. 5). Using this type of holder water cooling is not necessary. The relatively low surface temperature of the sample holder can lead to the formation of soot residues that are responsible for a dark colouring of the nitric acid. In most cases these organic residues can be oxidized by adding chloric acid to the nitric acid.

To remove the traces completely from the surface of the sample holder it is necessary to turn it upside down before starting the refluxing procedure so that the part holding the sample during the incineration immerges into the acid.

2.3. *Refluxing*

The elements released by the incineration are deposited on the quartz surfaces of the sample holder, of the burning chamber and of the cooling system. To dissolve these elements and to collect them in the test tube of the apparatus, 2 ml of an acid are boiled in the test tube. In the upper part the acid fumes condense on the water cooler and run back down through the combustion apparatus. The recovery is critically dependent on the duration of this refluxing: it is 90–95 % after 15 min and 95–100 % after 30 min.

The nature of the acid depends on the problem. In most instances nitric acid (65 %) is the most suitable. If it is necessary to oxidize organic residues after an incomplete incineration, a mixture of 1.5 ml of nitric acid and 0.5 ml of chloric acid/perchloric acid is used. For the determination of selenium it is advantageous to use hydrochloric acid (20,2 %), to reduce the selenate to selenite. For a determination of iodine acetic acid has been found useful. For the determination of non-metallic traces in organic matrices by ion-chromatography water is occasionally the only reagent used for refluxing [7].

Table 1. Recommended maximal sample amounts for samples which melt during the incineration. The sample is wrapped in two layers of filter paper

Matrix	Maximal sample weight (g)
India rubber	0.2
Polyacrylate	0.7
Polyvinylchloride	0.15
Glycerineester	0.1
Ointment with 6 % Bi	0.3
Shortening	0.2
Phenylmercury	0.1

2.4. *Sample Preparation*

The success of an incineration depends on the sample material and the size and form in which the sample is subjected to the incineration.

No larger quantities of volatile organic components must be set free during the combustion because this would cause crackling. Only up to 100 µl of liquid organic sample that evaporate during the combustion can be soaked into a filter paper. Some examples of these materials are listed in Table 1.

Materials not melting in the heat are preferably pressed to pellets. For the current investigations a press unit made of tungsten carbide based hard-metal ("Tizit")[3] is used. Thus contamination of the sample with trace metals is avoided. The compressed sample burns slowly and uniformly, so that up to 1 g (depend-

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ing on the matrix) can be burned (Table 2). The pellet has a diameter of 7 mm and a thickness of up to 18 mm. The ignition of the sample is accomplished by a small slice of filter paper used as matchcord. Aqueous samples, like blood or other body fluids, milk, fruit, juices and so on, are either soaked up with a filter paper and dried, or after freeze-drying pressed to a pellet.

Table 2. Recommended weight for various materials

Matrix	Sample weight (g)
Wood	1
Cellulose	1
Grass (dried)	0.8
Blood (freeze dried)	0.7
Milk powder	0.7
Flour	0.8
Coffee	0.8
Tea	0.8
Protein powder	0.7

3. Results and Discussion

To demonstrate the power of this new incineration device for practical work a couple of NBS-Standard Reference Materials were ashed and the elements B, Cr, Cu, Fe, Mn and Zn were determined by ICP-emission spectrometry, Cd and Pb by ETA-AAS, Hg by the AAS-cold vapor technique [2], As by the AAS-hydride method and Se by XRF [4]. The results are compiled in Table 3.

For a great number of organic samples, particularly for biological samples, the new ashing method is extremely powerful. As compared to other methods for decomposition the trace elements are recovered in a much lower volume, hence in a higher concentration, as only 2 ml of acid are used for up to 1 g of sample. The decomposition device described in this paper thus offers new possibilities for the extreme trace analysis of the elements. A drawback of the method is the low sample throughput of only one sample per hour.

Gross errors by incomplete recovery are practically not existent. Therefore, this incineration method is

Table 3. Analysis of NBS-Standard reference materials after incineration and refluxing with 2 ml HNO_3 (65%), 2 ml HCl (20.2%) for the determination of Se and 2 ml HNO_3 (65%)/0.5 ml $HClO_3 - HClO_4$ for the determination of Hg

Element		Content ± standard deviation µg/g ($N = 3$)						
		Wheat flour 1567	Rice flour 1568	Spinach 1570	Orchard leaves 1571	Tomato leaves 1573	Pine needles 1575	Bovine liver 1577
As	a		0.41 ± 0.05		10 ± 2	0.27 ± 0.05		
	b		0.41 ± 0.07		9.8 ± 0.1	0.25 ± 0.03		
B	a				33 ± 3			
	b				33.4 ± 0.7			
Cd	a			(1.5)	0.11 ± 0.01	(3)	(<0.5)	0.27 ± 0.04
	b			1.6 ± 0.2	0.11 ± 0.01	2.9 ± 0.1	0.31 ± 0.03	0.27 ± 0.05
Cr	a				2.6 ± 0.3		2.6 ± 0.2	
	b				2.8 ± 0.2		2.6 ± 0.2	
Cu	a	2.0 ± 0.3	2.2 ± 0.3		12 ± 1		3.0 ± 0.05	193 ± 10
	b	2.0 ± 0.1	2.1 ± 0.1		12.1 ± 0.2		3.0 ± 0.15	195 ± 10
Fe	a	18.3 ± 1	8.7 ± 0.6		300 ± 20		200 ± 10	268 ± 8
	b	19.3 ± 1.1	9.4 ± 0.3		317 ± 25		204 ± 12	269 ± 10
Hg	a		0.006 ± 0.0007					
	b		0.0056 ± 0.0005					
Mn	a	8.5 ± 0.5	20.1 ± 0.4		91 ± 4		675 ± 15	
	b	9.9 ± 0.5	21.4 ± 1.4		92.4 ± 0.8		678 ± 7	
Pb	a			1.2 ± 0.2	45 ± 3	6.3 ± 0.3	10.8 ± 0.5	0.34 ± 0.08
	b			1.1 ± 0.2	44 ± 4	6.2 ± 0.3	10.9 ± 0.3	0.35 ± 0.05
Se	a	1.1 ± 0.2	0.4 ± 0.1					1.1 ± 0.1
	b	1.10 ± 0.02	0.40 ± 0.02					1.1 ± 0.02
Zn	a	10.6 ± 1	19.4 ± 1		25 ± 3			
	b	11.3 ± 1.1	21.3 ± 1.3		28.5 ± 0.8			

a Certificated; b found

particularly suitable to double-check other decomposition methods that have a higher sample throughput.

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