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SCIENCE DIRECT
Talanta 68 (2006) 1736–1739
Talanta
www.elsevier.com/locate/talanta

Short communication

Oxidative extraction versus total decomposition of soil in the determination of thallium

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Received 13 May 2005; received in revised form 25 July 2005; accepted 10 August 2005
Available online 28 October 2005

Abstract

An aqua regia extraction and a total decomposition of soil were compared in terms of thallium determination. A sequential extraction of soil, according to the BCR protocol, was also performed for additional information on thallium distribution in soil fractions. Certified reference material—soil GBW 07401 of Chinese origin, containing 1 ± 0.2 ppm of thallium was used in these experiments. Thallium was determined by flow injection-differential pulse-anodic stripping voltammetry (FI-DP-ASV). Only 35% of total thallium was extracted in the aqua regia extraction, while the total decomposition led to satisfactory recovery. The sequential extraction showed that only 5% of thallium in GBW 07401 is dissolvable in the four BCR procedure fractions, and that 95% of the element is entrapped in the residual parent matter. These results show that the aqua regia extraction does not ensure complete thallium extraction from soil. Surprisingly, the total decomposition is significantly less time consuming than the aqua regia extraction.

Keywords: Thallium; Soil; Total decomposition; Aqua regia extraction; Sequential extraction; Flow injection-differential pulse-anodic stripping voltammetry

1. Introduction

Oxidative extraction significantly facilitates the determination of elements in soil, and equally significantly, oxidative extraction reduces the cost of a single determination. In the case of the majority of elements, aqua regia extracts of soil contain virtually whole elements occurring in a sample. Therefore, the concentration of an element in aqua regia extracts is used as the total concentration of an element in the sample. However, this is not so obvious for thallium in soil, although aqua regia extracts were used for this purpose [1]. Lukaszewski and Zembrzuski [2] reported that thallium recovery in an aqua regia procedure, for different samples, ranges between 21 and 74% of the total content (determined by complete decomposition). On the other hand, Tremel et al. [3] reported that oxidative extraction solubilizes thallium completely. In order to avoid thallium loss due to the volatility of $TlCl_3$, a mixture of 14 M nitric acid and 30% hydrogen peroxide, with heating under reflux was used, as well as a soil standard reference material, in order to control the correctness of the procedure. It may be possible that part of the soil may have thallium entirely extractable during the oxidative procedure and the other part may have thallium strongly entrapped in primary geological material and therefore may not be extractable. Therefore, this difference may be a measure of the general mobility of the element.

The aim of this paper was to compare the results of aqua regia extraction of thallium from soil and that of a total decomposition with hydrofluoric acid used for mineral matrix destruction. The objective of the investigation was the certified reference material—soil GBW 07401 of Chinese origin, containing 1 ± 0.2 ppm of thallium. Apart from this comparison, the sequential extraction of this soil, according to the BCR procedure [4] was performed with the determination of thallium in the fractions. These data provided more precise information concerning the thallium mobility. Thallium was determined by flow injection-differential pulse-anodic stripping voltammetry (FI-DP-ASV) [2]. This method ensures the high sensitivity and selectivity of thallium determination [2]. The composition of the base electrolyte (0.05 M EDTA, pH 4.4) ensures a high tolerance for the presence of lead and cadmium. One thousand-fold excess of lead is tolerated [6]. Interferences of the main elements of the soil matrix such as iron can be removed by

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doi:10.1016/j.talanta.2005.08.035

a medium exchange after a preconcentration stage. The interference problem was broadly discussed in previous papers [2,6]. Ten picomole of thallium can be determined by the method.

2. Experimental

2.1. Apparatus and reagents

An Ecochemie (Utrecht, The Netherlands) electrochemical analyser MICROAUTOLAB was used together with a previously described [2] flow-through cell of a wall-jet type, which facilitates medium exchange and medium circulation. The differential-pulse amplitude was 50 mV. The mercury film electrode based on epoxy resin impregnated graphite was used as a working electrode, a saturated calomel electrode was the reference electrode and platinum wire was the auxiliary electrode. The mercury film was deposited over a period of 10 min from the solution consisting of 0.05 mM mercury(II) nitrate and 0.1 M potassium nitrate. Only one mercury film was required for a whole day of measurements.

Certified reference material—soil GBW 07401 of Chinese origin, containing 1 ± 0.2 ppm of thallium was used.

All solutions were prepared in water, prepared by reverse osmosis in a Watek–Demiwa 5 rosa system (Czech Republic), followed by triple distillation from a quartz apparatus. Only freshly distilled water was used.

2.2. Procedures

2.2.1. Aqua regia extraction of soil

This procedure was performed in accordance with a slightly modified procedure of Wolf et al. [5]. The soil sample (approximately 0.5 g) was placed in a test tube equipped with a reflux condenser and treated with 20 ml of aqua regia (3:1 mixture of 37% hydrochloric acid and 65% nitric acid) and put aside for 48 h. The sample was then heated for 2 h and filtered. The filter was washed with 2 M nitric acid and the filtrates mixed. The solution was evaporated in a fused-silica beaker. In the final stage of evaporation, five 0.5 ml portions of 30% hydrogen peroxide were added to completely mineralise any organic matter. The residue was then dissolved in 1 ml hydrochloric acid. The solution of ascorbic acid in the amount corresponding to the final concentration of 0.1 M was added and after a few minutes the corresponding amount of EDTA solution was added. The pH was adjusted to 4.5 with ammonia and the solution transferred into a 25 or 100 ml volumetric flask and supplemented with water.

2.2.2. Total decomposition of soil

The soil sample (approximately 0.25 g) was placed in a high teflon beaker, moistened with water, treated with 2 ml of 73% hydrofluoric acid and put aside for 2 h. At the end of this period, an additional 0.6 ml of hydrofluoric acid was added. The obtained solution was heated on a graphite heater until evaporated. One millilitre of 67% nitric acid was then added, as well as 2.5 ml of 30% hydrogen peroxide in 0.5 ml portions, for the mineralisation of residual organic substances. The sample was evaporated after addition of each hydrogen peroxide portion. Finally, 1 ml of nitric acid was added, the beaker covered with a watch glass and heated for 3 h. A 2.5 ml of 1 M ascorbic acid and 6.25 ml of 0.2 EDTA were then added and the pH was adjusted to 4.5 with ammonia, the solution was transferred into a 25 volumetric flask and supplemented with water.

2.2.3. Sequential extraction of soil

This procedure was performed in accordance with the modified BCR procedure [4].

2.3. Water soluble fraction

The soil sample (1.00 g) was treated with 40 ml of demineralised water in a 100 ml conical flask and shaken at 25 °C for 16 h. The mixture was centrifuged and the solution transferred into a 100 ml volumetric flask. Twenty five millilitre of 0.2 M EDTA was added and the flask supplemented with water to the mark.

2.4. Acid soluble/exchangeable fraction

The sample was treated with 40 ml of 0.11 M acetic acid in a 100 ml conical flask and shaken at 25 °C for 16 h. The mixture was then centrifuged and the solution transferred into a 100 ml volumetric flask. The soil sample was treated with 10 ml of water and shaken for 10 min and then centrifuged and the solution added to the solution of the fraction. The pH of solution was adjusted to 4.5 with 25% aqueous ammonia solution or 2 M nitric acid, 25 ml of 0.2 M EDTA was added and the flask supplemented to the mark with water.

2.5. Reducible fraction

The sample was treated with 40 ml of 0.1 M hydroxylamine hydrochloride adjusted to pH 2 with 2 M nitric acid in a 100 ml conical flask and shaken at 25 °C for 16 h. The mixture was centrifuged and the solution transferred into a 100 ml volumetric flask. The soil sample was treated with 10 ml of water and shaken for 10 min and centrifuged. The solution was added to the solution of the fraction. Ten millilitre of 1 M ascorbic acid was added to the joint solutions. The pH was adjusted to 4.5 with 25% aqueous ammonia solution or 2 M nitric acid, 25 ml of 0.2 M EDTA was added and the flask supplemented to the mark with water.

2.6. Oxidisable fraction

The sample was treated with 10 ml of 30% hydrogen peroxide in a 100 ml conical flask and shaken at 25 °C for 1 h and at 85 °C for the following 1 h. The mixture was evaporated to the volume of 1–2 ml. The next 10 ml portion of 30% hydrogen peroxide was added, the mixture shaken at 85 °C for 1 h, and the mixture evaporated until dry.

The residue was treated with 50 ml of 1 M ammonium acetate adjusted to pH 2.0 with 2 M nitric acid and shaken at 25 °C for 16 h. The mixture was centrifuged and the solution transferred into a 100 ml volumetric flask. The soil sample was treated with

10 ml of water and shaken for 10 min and centrifuged. The solution was added to the solution of the fraction. Ten millilitre of 1 M ascorbic acid was added to the joint solutions. The pH was adjusted to 4.5 with 25% aqueous ammonia solution or 2 M nitric acid, 25 ml of 0.2 M EDTA added and the flask supplemented to the mark with water.

2.7. Entrapped parent matter fraction

A residue of the sample was processed as described in Section 2.2.2.

2.8. Determination of thallium by the FI-DP-ASV

Determination was performed in accordance with the procedure described previously [2]. Thallium preconcentration was performed at a potential of −900 mV versus SCE over 60–1200 s, depending on thallium concentration. Voltammograms were recorded after the medium exchange on pure 0.05 M EDTA. The results were evaluated on the basis of several standard additions (typically three additions).

3. Results and discussion

Five parallel samples of the soil GBW 07401 were processed in accordance with the aqua regia extraction protocol (described above) and nine parallel samples were processed with the total decomposition protocol (also described above). Thallium in extracts, or in dissolved samples, was determined by means of the FI-DP-ASV. Three measurements were performed with each solution. The results are given in Table 1. In order to demonstrate an 'instrumental' precision, examples of experimental series are given in Table 2. For every soil sample, two series of measurements are given: one series is the most typical in terms of precision and the second series is the worst.

It is clear that only 35% of total thallium is extracted in the aqua regia extraction because the certified thallium concentration is 1 ± 0.2 ppm. On the other hand, total decomposition leads to satisfactory recovery. The precision of thallium determination in the whole procedure is similar in both procedures, i.e. 11–12%. The 'instrumental' precision, i.e. the precision of thallium determination in obtained solutions is significantly better and even in the worst series is 1.6% for the total decomposition and 3.8% for aqua regia extracts. Thus, the main source of the precision error is the sample extraction or decomposition.

Table 1
Concentration of thallium (ppm) in the GBW 07401 soil as determined with the total decomposition of sample or aqua regia extraction

Sample	Total decomposition	Aqua regia extraction
A	1.1	0.34
B	0.99	0.30
C	0.88	0.39
D	0.97	0.31
E	0.85	0.39
F	0.95	
G	0.97	
H	0.83	
I	0.78	
Average	0.92	0.35
S.D.	0.098	0.043
R.S.D. (%)	10.6	12.2

Table 2
Concentration of thallium (ppm) in the GBW 07401 soil as determined with the total decomposition of sample or aqua regia extraction

	Total decomposition	Aqua regia extraction
Typical series	0.99	0.33
	1.0	0.34
	0.99	0.34
Average	0.99	0.34
S.D.	0.006	0.006
R.S.D. (%)	0.6	1.8
The worst series	0.96	0.39
	0.97	0.41
	0.99	0.36
Average	0.97	0.39
S.D.	0.016	0.015
R.S.D. (%)	1.6	3.8

Examples of experimental series.

A significant question arises why Tremel et al. [3] were able to extract whole thallium from the certified soil sample in the oxidative extraction procedure. They determined 2.403 ppm of thallium in the NIST soil (no. 2711) certified as containing 2.470 ± 0.150 ppm thallium. Certainly, the NIST no. 2711 soil contains only extractable thallium, while in the case of the GBW 07401 soil the major part of thallium is not extractable. The conclusion can be drawn that thallium extractability from soil during the oxidative extraction cannot be presumed without checking.

In order to investigate in which fraction of the GBW 07401 soil thallium is bounded, the sequential extraction of five parallel samples of this soil were processed in accordance with the BCR protocol [4]. Water (water soluble fraction), 0.11 M acetic acid (acid soluble/exchangeable fraction), 0.1 M hydroxylamine hydrochloride (pH 2; reducible fraction) and 30% hydrogen peroxide (oxidisable fraction) were used as extractants. The residue was decomposed in the same way as the soil sample. The results are shown in Table 3.

It is clear that approximately only 5% of thallium is soluble during the procedure and is located mainly in reducible and oxidisable fractions and the majority of the element is insoluble as it is entrapped in the parent matter. These results support the conclusion that the majority of thallium is strongly bonded to the parent matter and is not mobilised during oxidative extraction. Water and acid soluble/exchangeable fractions contain only 0.5% of the total thallium of the soil. Only this part of the element is readily mobile.

It is worth stressing that the total decomposition of the soil sample is significantly faster than the aqua regia extraction. A comparison of time consumption at particular steps of both procedures is shown in Table 4. A passive time, when a sample is left, is considered separately from an active time when opera-

Table 3
Thallium concentration (ppb) in the GBW 07401 soil fractions

Sample	Fraction					Total
	Water soluble	Acid soluble/exchangeable	Reducible	Oxidisable	Entrapped parent matter	
A	1.5	3.0	20	25	750	800
B	2.3	2.0	19	28	890	940
C	1.5	3.1	23	21	800	840
D	1.2	2.9	23	30	810	860
E	1.2	3.3	19	20	840	880
Average	1.5	2.9	21	25	820	870
S.D.	0.5	0.5	2.0	4.3	52	52
% of total Tl	0.2	0.3	2.4	2.9	94.2	100

Obtained by sequential extraction in accordance with the BCR protocol.

Table 4
Comparison of time consumption on the total decomposition and aqua regia extraction of soil samples

Total decomposition				Aqua regia extraction			
Active time		Passive time		Active time		Passive time	
Weighting	10 min			Weighting	10 min		
Treatment with hydrofluoric acid	2 min	Treatment with hydrofluoric acid	2 h	Treatment with aqua regia	2 min	Treatment with aqua regia	48 h
		Evaporation	2 h			Heating	2 h
Mineralisation and evaporation	60 min			Filtration	30 min		
Solution of residue	2 min	Solution of residue	3 h			Evaporation	2 h
Preparation of final solution	10 min			Mineralisation and evaporation	60 min	Mineralisation and evaporation	2 h
FI-DP-ASV measurement	60 min			Solution of residue	10 min		
				Preparation of final solution	10 min		
				FI-DP-ASV measurement	60 min		
Total	2 h 24 min		6 h		3 h 2 min		54 h

tions with the sample are in process. The aqua regia extraction requires 3 h of active time and 54 h of passive time, while the total decomposition requires only 2.5 h of active time and 6 h of passive time. The protocol of Tremel et al. also requires a minimum 2 h of active time and 18 h of passive time. Thus, the presumed main advantage of the aqua regia extraction or extraction with nitric acid–hydrogen peroxide, i.e. the reduction of time for analysis is not well-founded in the case of thallium determination in soil.

Acknowledgement

This work was supported by the Polish Ministry of Scientific Research and Information Technology (Institutional grant for the Faculty of Chemical Technology, Poznan University of Technology, grant no. 31 DS 31-086/05).

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