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Determination of Arsenic, Mercury and Barium in Herbarium Mount Paper using Dynamic Ultrasound-Assisted Extraction prior to Atomic Fluorescence and Absorption Spectrometries

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Abstract

A dynamic ultrasound-assisted extraction method using Atomic Absorption and Atomic Flourescence spectrometers as detectors was developed to analyse mercury, arsenic and barium from herbarium mount paper originating from the herbarium collection of the National Museum of Wales. The variables influencing extraction were optimised by a multivariate approach. The optimal conditions were found to be 1% HNO_3 extractant solution used at a flow rate of 1 mL min^{-1}. The duty cycle and amplitude of the ultrasonic probe was found to be 50% in both cases with an ultrasound power of 400 W. The optimal distance between the probe and the top face of the extraction chamber was found to be 0 cm. Under these conditions the time required for complete extraction of the three analytes was 25 min.

Cold vapour and hydride generation coupled to atomic fluorescence spectrometry was utilized to determine mercury and arsenic, respectively. The chemical and instrumental conditions were optimized to provide detection limits of 0.01ng g^{-1} and 1.25 ng g^{-1} for mercury and arsenic, respectively. Barium was determined by graphite-furnace atomic absorption spectrometry, with a detection limit of 25 ng g^{-1}. By using 0.5 g of sample, the concentrations of the target analytes varied for the different types of paper and ranged between 0.4–2.55 µg g^{-1} for Ba, 0.035–10.47 µg g^{-1} for As and 0.0046–2.37 µg g^{-1} for Hg.

Keywords: mercury, arsenic, barium, ultrasound extraction, Atomic Spectroscopy, remediation

1. Introduction

The presence of heavy metals in museum natural history collections has been raising concerns for a number of years. Toxic metals, such as arsenic and mercury, are present as residues of past biocide treatments applied to prevent the degradation of the organic material within the collections. The presence of these residues raises health and safety issues for staff and visitors handling the collections. From the early eighteenth century, a variety of different biocide recipes have been used, including mercuric chloride, lead hydrogen arsenate, arsenic trioxide and barium fluorosilicate. Although these treatments, and the recipes used, are recorded -for example, in different taxidermy handbooks (Marte et al. 2006)-, records of specific biocide applications within collections are sporadic, making identification of those likely to be contaminated difficult. With large collections (the National Museum of Wales herbarium (NMW) houses c. 250,000 higher plant specimens), it is not feasible, nor cost-effective, to identify contamination through analysing the whole collection. Current research at the University of Lincoln (Purewal et al. 2008) aims to develop a rapid screening method for these large collections, providing a means to prioritise which collections require immediate re-mounting, to inform the implementation of standard procedures to protect personnel and visitors handling the collections, and to enable the removal of a large amount of hazardous chemical from the herbarium environment. As part of this work, the analysis of trace levels of mercury, arsenic and barium within a paper matrix is essential. Mercury toxic levels vary depending on the chemical state of the metal and exposure, but effects on humans have been reported at concentrations as low as 10.5 μg L^{-1} (Yang et al. 1994). Mercury distributes to all tissues and accumulates in the brain. Known effects are neurological damage, cancer, cardiovascular damage and renal and hepatic problems. Arsenic produces different symptoms from nausea at low levels to acute poisoning to death when concentrations are above 500 μg L^{-1}. Chronic exposure can produce skin, lung or liver cancer (Jickells and Negrusz 2008). Most insoluble salts of Barium are non toxic, but soluble ones are extremely toxic and an oral fatal dose is as little as 0.8 g in humans. In some cases of non fatal poisoning, blood concentrations up to 8 mg L^{-1} have been reported (Boehnert 1988).

There are many analytical methods suitable for the analysis of these metals. Arsenic (Saraswati et al. 1995) and mercury (Zhang and Adeloju 2008) can be subjected to hydride generation and cold vapour generation, respectively, prior to atomic absorption spectrometry, although inductively coupled plasma mass spectrometry (ICP–MS) tends to be the favourite analysis technique in many cases, due to its multi-elemental analysis capability and low

detection limits (Özden 2008). The main shortcomings ICP-MS faces at present are both the high acquisition costs and, more importantly, expensive maintenance owing to high gas consumption. An alternative more economical technique to ICP–MS is vapour generation atomic fluorescence spectrometry. This approach provides similar analytical performance for mercury and hydride forming elements with superior selectivity and linearity. AFS has proved to be effective for the analysis of these metals in different matrices after proper extraction of the target species (Priego-López and Luque de Castro 2002; Fernández-Pérez et al. 2000; Fernández-Pérez et al. 1999). Barium can be easily analysed in different matrices using atomic absorption spectrometry (AAS) with (Kalny et al. 2007) or without graphite furnace (Jaiswal et al. 2006).

The preferred sample preparation technique prior to determination of metals in most matrices is digestion, which can be implemented using different approaches (Marte et al. 2006). In the case of arsenic and mercury special care must be taken as some species of these analytes are volatile and losses during the sample preparation step can be significant.

Some approaches, which have provided good efficiencies for the isolation of arsenic and mercury from solid matrices, are focused microwave-assisted Soxhlet extraction (Fernández-Pérez et al. 2000) and subcritical water extraction (Priego-López and Luque de Castro 2002; Luque de Castro and Priego-Capote 2006), among others (Marte et al. 2006). A very promising alternative energy to accelerate extraction is ultrasound (Luque de Castro and Priego-Capote 2006), which has been proved effective for the extraction of different metals in matrices such as cotton (Rezić 2009), sediments and soil (Collasiol et al. 2004) and biological tissues (Krishna et al 2005).

The main aim of this study was to develop an alternative method to the existing ones based on extraction assisted by ultrasound and atomic spectroscopy for the removal of mercury, arsenic and barium from contaminated mount paper from the NMW herbarium. To the best of our knowledge, ultrasound extraction has never been reported for the extraction of contaminated paper or any other museum material. The use of vapour generation coupled to atomic fluorescence spectrometry for the determination of arsenic and mercury in this kind of sample is also scarce.

2. Experimental

2.1 Instruments and apparatus

Ultrasonic irradiation was applied by means of a Branson 450 sonifier (20 kHz, 400 W) equipped with a cylindrical titanium alloy probe (12.7mm diameter) which was immersed in a water bath in which the extraction cell was placed. An extraction chamber consisting of a stainless steel cylinder (5 cm in length and 1 cm i.d.), closed with screws at either end, was used, allowing circulation of the leaching solvent at a controlled flow rate. The screw caps were covered with stainless steel filter plates to ensure that the sample remained in the extraction chamber. Despite the sample coming into contact with the stainless steel cylinder no contamination problems or losses of analyte were found. This was validated by performing extractions on spiked paper samples and also blank extractions using the optimal working conditions. A Gilson Minipuls-3 low-pressure peristaltic pump, programmed for changing the rotation direction at preset intervals, and PTTE tubing of 0.8 mm i.d. were used to construct the flow manifolds for sample extraction. The pump was operated through a personal computer and associated software.

Mercury determinations were conducted using a PSA 10.025 Millennium Merlin continuous flow cold vapour generation using tin (II) chloride reduction with atomic fluorescence spectrometry. This device is described in more detail elsewhere (Reis et al. 2003)

A PSA 10.055 Millennium Excalibur hydride generation atomic fluorescence spectrometer equipped with boosted discharge hollow cathode lamp operated at 27.5 mA primary and 35.0 mA boost current was utilized to determine arsenic (Moreno et al. 2000). Hydride generation was performed using a sodium tetrahydroborate (III) reductant after pre-reduction of arsenate to arsenite using potassium iodide. Atomization of the gaseous hydride was achieved using an argon-hydrogen diffusion flame fuelled by the excess hydrogen produced from the decomposition of the $NaBH_4$ reagent.

A Varian SpectrAA 110 atomic absorption spectrometer furnished with an electrothermal atomizer (ETA), and equipped with a Varian GTA 110 autosampler was used for barium determination. A Varian hollow-cathode lamp was used as radiation source. The lamp current was at 20 mA and the monochromator set at 553.6 nm.

2.2 Chemicals and samples

Ultrapure water from a Milli-Q system from Millipore, (Bedford, USA) was used throughout. All glassware and bottles used were cleaned in 4 M HNO_3 for 4 days and rinsed with high-

purity water before use. Analytical grade 65% HNO_3 (Panreac, Barcelona, Spain) was used for preparation of the leaching carrier (1% HNO_3).

Individual stock solutions of 1 g L^{-1} As (III), Hg (II), and Ba (II) from Fluka (Buchs, Switzerland) were prepared and, from these, the standard working solutions were prepared immediately before use by dilution with water or the appropriate reagent blank for the vapour generation system.

Sodium tetrahydroborate (III) reducing reagent was prepared daily at 0.7% (w/v) from Sigma (St. Louis, USA) stabilised in 0.1 mol L^{-1} NaOH. The reagent blank for the hydride generation system was 30% (v/v) HCl (Panreac) with 2% (v/v) of the pre-reducing agent (50% w/v KI in 10% w/v Ascorbic acid).

After the results of the optimisation process, Tin (II) chloride at 1% (w/v) (Merck) prepared in 10% v/v HCl was used to reduce Hg (II) to elemental Hg. The reagent blank for cold vapour generation system was 10% HCl.

Argon (Carburos Metálicos) was used as the protective gas in the ETAAS determination procedure and also as carrier gas for the vapour generation systems.

Four herbarium mount papers were obtained from the NMW (succession nos. 28·131·2095, 28·131·20956, V·2008·2-991 and V·2008·4-1486). The specimens had been previously removed and remounted.

2.3 Sample preparation

Each mount paper was divided into eight sections and a letter assigned to each as illustrated in Fig. 1. The sections were then cut into approximately 2.5 cm squares and stored separately in labelled plastic containers. A sample of 0.5 g was removed from each section and subjected to ultrasound-assisted extraction.

2.4 Proposed method

2.4.1Extraction procedure.

Prior to ultrasound extraction, each 0.5 g spiked paper was weighed and placed in the extraction chamber of the dynamic approach in Fig. 2, which was assembled and filled with the leaching carrier (1%v/v HNO_3) impelled by the peristaltic pump. After filling, the extraction chamber was immersed into the water bath at room temperature (20^{o}C), maintained during the extraction time. As the methodology is developed in a closed-system,

analyte losses were kept to a minimum. The extractant carrier was then circulated through the solid sample for a period of 25 minutes under ultrasonic irradiation (duty cycle 0.5 s, output amplitude 50% of the converter, applied power 400 W with the probe placed at the top surface of the extraction cell). During extraction, the direction of the carrier (at 1 mL min^{-1}) was changed each 120 s, thus minimising the compactness of the sample in the extraction cell that could cause overpressure in the system. Once the extraction time was completed the leaching carrier was removed from the system and diluted to 10 mL with 1% v/v HNO_3.

2.4.2 Determination procedures.

Barium was determined by ETAAS after extraction under the working conditions shown in Table 1.

Arsenic and mercury were determined using vapour generation atomic fluorescence spectrometry (AFS). For arsenic measurements a pre-reduction was used to convert arsenate to arsenite prior to hydride generation. The pre-reduction was found to take approximately 30 minutes at room temperature. The reduced sample was injected into a HCl carrier in the manifold as shown in Figure 3. The working conditions for this determination are in Table 2. The volatile hydride formed was swept out of the gas–liquid separator by an argon stream into the chemically generated hydrogen diffusion flame. The hydride was atomised in the flame and detected by fluorescence spectrometry.

The manifold to form cold vapour from Hg(II) and subsequent AFS detection was the same as for As (Fig. 3). The Hg(II) was reduced to Hg(0) by a $SnCl_2$ stream and swept out of the gas–liquid separator by an argon stream into the atomic fluorescence detector. The volume injected was 100 μL in both cases.

3. Results and Discussion

3.1 Optimisation of the method

3.1.1 Optimisation of the formation of volatile species. A half-fractioned design type IV resolution was applied, involving 8 experiments plus 3 centre points for optimization of the four factors (acid concentration of the carrier, concentration of the reductant agent — sodium borohydride for As and tin chloride for Hg — and flow rates of the liquid phase and carrier gas). The conclusions of this study showed that only the flow-rates of the liquid phase and carrier gas are statistically influential factors and lower and higher flow rates should be

studied for the donor and acceptor phases, respectively. However, it was also shown that the best results were obtained when high acid concentration of the carrier solution and low concentration of the reductant agent were used — namely, 6% and 2%, respectively. These values were, therefore, selected for subsequent experiments. A response surface for these variables yielded 1.50 mL min^{-1} and 325 mL min^{-1} as optimal values for the liquid phase and carrier gas flow rate, respectively. The same optimum flow rates were obtained for both As and Hg as shown in table 2.

3.1.2 Optimisation of the extraction step. For optimisation of this step, seven variables were considered, namely: the probe position, ultrasound radiation amplitude, percentage of duty cycle of ultrasound exposure, irradiation time, flow-rate, composition and volume of the extractant. The latter was studied by changing the coil length. The response variable was the concentration for each metal as determined under optimal conditions previously determined.

A Plackett–Burman design $2^7 \times 3/32$ type III resolution allowing four degrees of freedom and involving 12 randomised runs plus three centre points was built for a screening study of the behaviour of the seven factors affecting the extraction process. The upper and lower values given to each factor were selected from the available data and experience gathered in the preliminary experiments. The tested and the optimum values obtained for each variable are shown in Table 3.

The conclusions of this screening study were that none of the factors were statistically influential within the studied ranges, except the extraction time. However, the results showed better extraction efficiencies with the minimum value of extractant flow-rate, probe position, composition of the extractant and percentage of duty cycle of ultrasound exposure and maximum values of the other three variables. Thus, the lowest value tested for the flow-rate, probe position, composition of the extractant and percentage of duty cycle of ultrasound exposure (namely, 1 mL min^{-1}, 0 cm, 1% and 10%, respectively) and the highest values tested for the ultrasound radiation amplitude and the extractant volume (namely, 50% and 2 mL, respectively) were selected for subsequent experiments.

A kinetics study was developed in order to determine the time required for complete extraction of the target analytes by keeping the other variables at their optimum values (see Table 3). Complete extraction was achieved within 25 min.

3.2 Application of the method

Paper spiked with the three elements was used to calculate the recoveries using ultrasound extraction. The final concentration of each element in the 15.7 cm x 10.8 cm spiked paper was As 2.33 μg g^{-1} (91 % recovery), Hg 1.85 μg g^{-1} (93% recovery) and Ba 1.40 μg g^{-1} (87% recovery). Using standardised samples the analytical limits of detection and quantification, precision (sample concentration ranging from 10 ppb to 100ppb) and calibration curves were also calculated. Table 4 summarises all the results obtained for these analytical characteristic of the method.

The proposed method was applied to papers donated by the National Museum of Wales from the nineteenth and early twentieth centuries. A faint darkened area was visible on some of the papers that under a certain light appeared to be the outline of leaves. Strips of tape were also present on the papers that had presumably been used to secure the plant in a given position.

Figure 4 shows the results obtained by application of the proposed method, which are also summarised in Table 5. The variance obtained in the analysis of the target metals in the different pieces of the same paper is likely due to the method of biocide application – dipping of specimen prior to mounting; brushing, spraying or sprinkling of powders over mounted specimens- rather than lack of reproducibility in the method. This is supported by precision data as can be seen in table 4. Due to the nature of the material, sample replicates were not possible. It seems that the sections of the paper which were covered by plant material have lower metal concentration than those which are uncovered. Furthermore, this variability is greater for mercury followed by arsenic and barium. The lower variability found for barium may be indicative of its use in the paper manufacture at that time rather than as a biocide.

In terms of concentration, lower levels of mercury were found on the papers than either barium or arsenic. This may reflect the relative historic use of these metals as biocides, or may be indicative of their respective longevities within the collection – there is evidence to suggest that the degradation of paper reduces Hg(II) to Hg(0) over time, with subsequent loss of mercury to the atmosphere. In all cases, the four papers analysed showed differences in the amounts of biocides they contained. As shown in table 4, the amounts of studied metals determined in the paper specimens greatly differ, making an overall estimate of the problem difficult. The average size of the mounting paper was 25 x 40cm with an average weight of 50g. Using table 5, the following approximated average concentrations can be therefore established: Hg (17 μg average per paper sheet), As (194 μg per paper sheet) and Ba (49 μg per paper sheet). Considering the amount of these materials stored in collections all across the UK, replacement and subsequent disposal may represent a health and environmental problem.

In our study each mount sheet was found to contain toxic levels of the different metals analysed. Ultrasound extraction can be considered as an alternative both for the analytical extraction prior to determination and remediation of the contaminated paper for their safe and rapid disposal. In this sense, a larger scale system than the one used in this paper could quickly, safely and economically remove much higher amounts of biocides and transform the solid residue into a liquid residue, easier to treat. The use of diluted nitric acid in the extraction readily allows neutralisation of the exhausted solid residue obtained after the extraction for its safe disposal.

4. Conclusion

A novel method based on ultrasound-assisted extraction and ulterior determination of arsenic, mercury and barium in paper by atomic absorption spectroscopy and atomic fluorescence spectrometry has been developed. Following extraction, atomic absorption spectrometric analysis of sample papers for barium showed a quasi-homogenous distribution over the entire area of each paper, indicating either an even application of biocide or, more likely, the inclusion of barium in the paper manufacture process. Mercury and arsenic showed a different concentration in all four paper samples, although the response within the paper can be considered almost homogeneous. This may reflect different papers being exposed to solutions containing different metal amounts, but may also be indicative of the different behaviour of these residues on a degrading substrate. On average, the amounts of metals present in the paper specimens were found to be toxic. Ultrasound extraction successfully removed the metals from the paper matrix, offering a cheap and quick method to extract these metals from solid paper waste before disposal.

5. Acknowledgements

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FIGURE LEGENDS

Fig. 1 A photograph of V·2008·4(1486). The positioning of the sections is illustrated together with the brown staining from the plant and absent regions of paper

Fig. 2 Approach used for ultrasound-assisted extraction of As, Hg and Ba from paper

Fig. 3 Dynamic approach for chemical vaporisation (As hydride) and cold atomic vapour formation (Hg) prior to fluorescence detection. The carrier solution was HCl in both cases and $NaBH_4$ or $SnCl_2$ were used as reagent (reductant) for As and Hg, respectively

Fig. 4 Different metal concentrations in the analysed paper samples

Table captions

Table 1. Values of the instrumental parameters for the determination of Ba by ETAAS

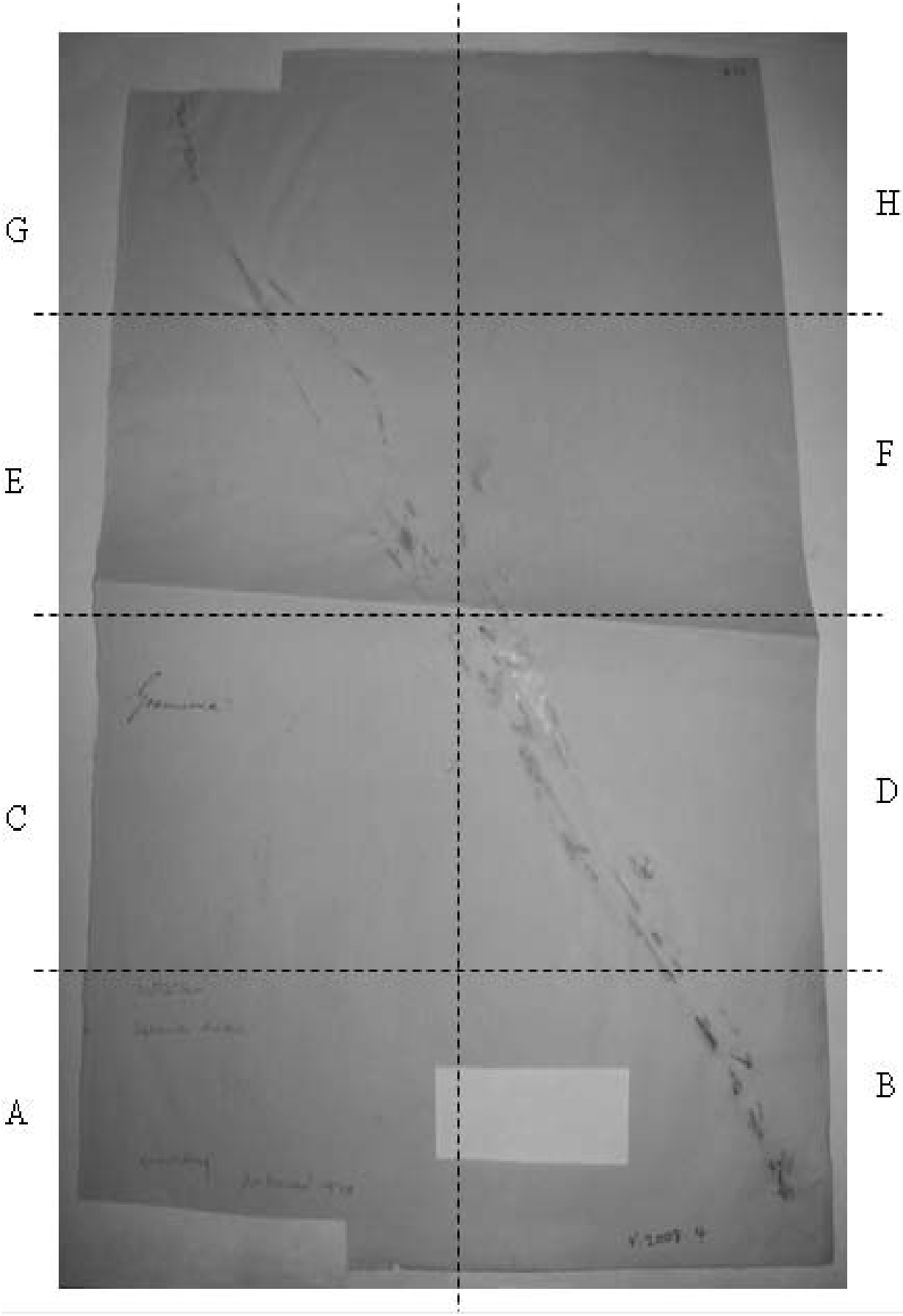
Table 2. Optimisation of the formation of volatile species prior to the determination of mercury and arsenic by atomic fluorescence spectrometry

Table 3. Optimisation of the ultrasound-assisted extraction step

Table 4. Summary of the analytical properties for the different metals

Table 5. Results showing the content of the metals in the whole paper sheet as an average of the different sections analysed (differences between them are expressed as %RSD)

1 Figure 1



2

Figure 2

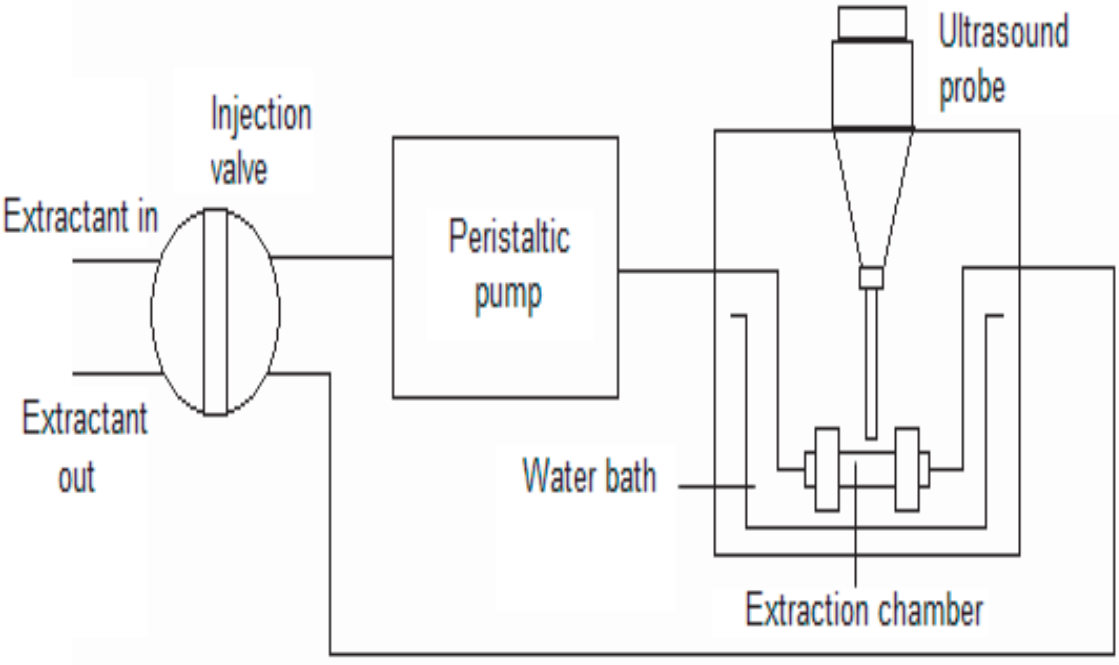


Figure 3

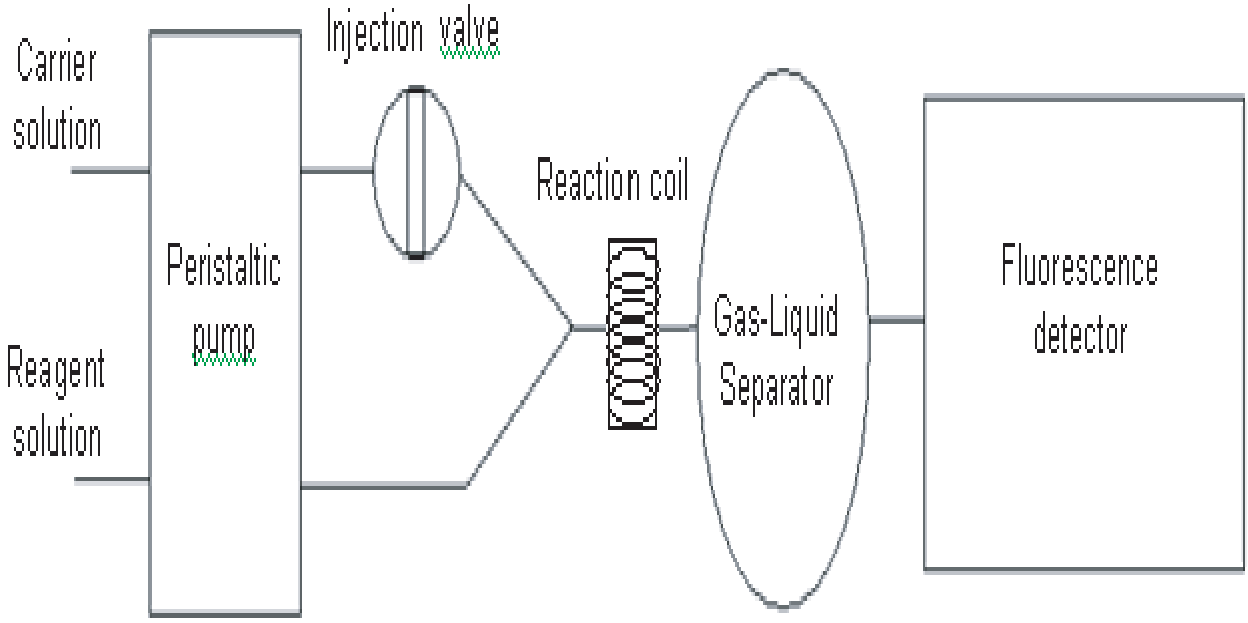
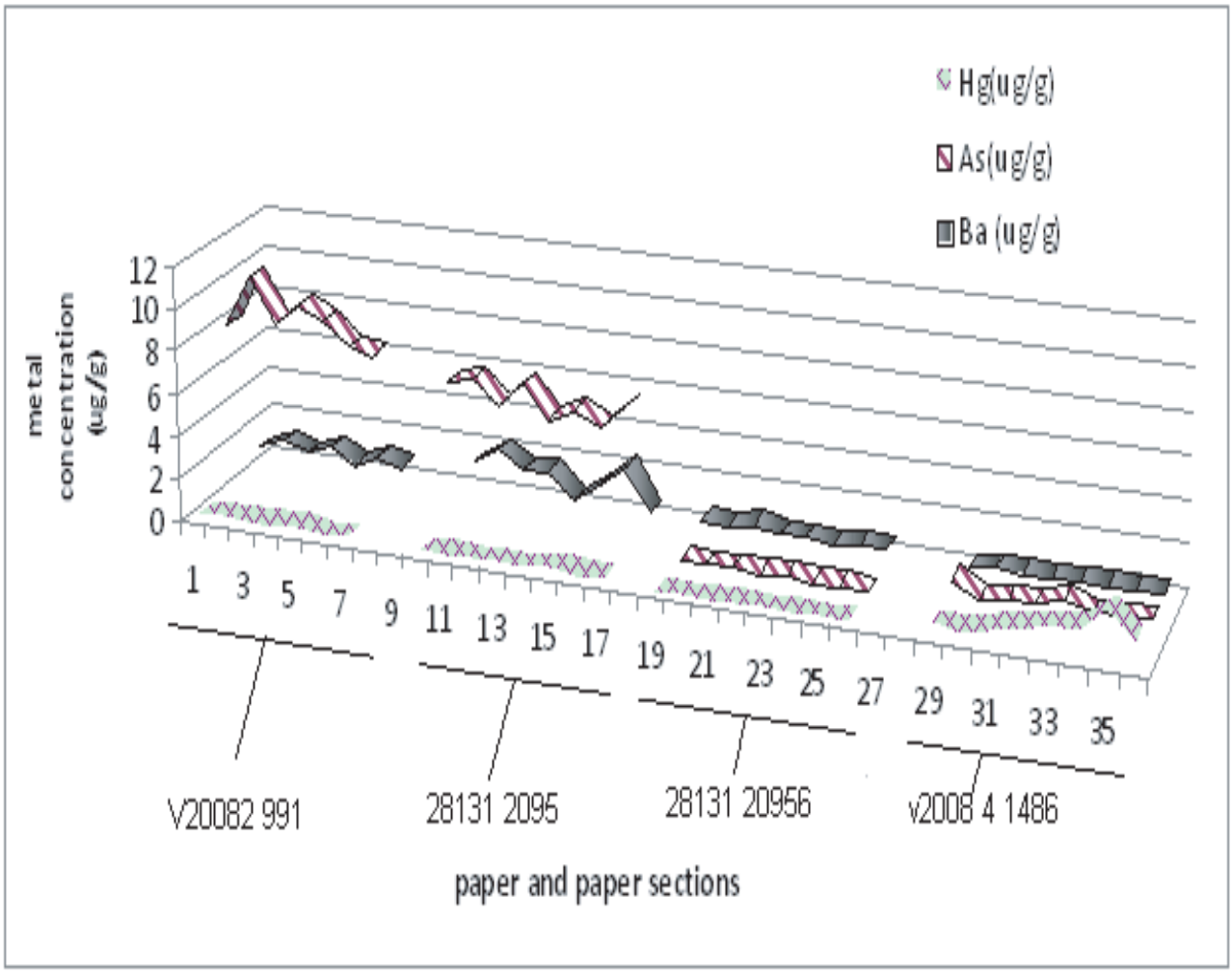


Figure 4


Hg(ug/g)
As(ug/g)
Ba (ug/g)
metal concentration (ug/g)
0
2
4
6
8
10
12
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35
V20082 991
28131 2095
28131 20956
v2008 4 1486
paper and paper sections

Tables

Table 1

Parameter (ETAAS)	Ba
λ(nm)	553.6
SW(nm)	0.4
T dry stage (ºC)	115
Time (s)	42
T ash stage (ºC)	1200
Time (s)	30
T atomisation stage (ºC)	2550
Time (s)	5.0

Table 2

Variables	**Range investigated**	**Optimum value**
[HCl] (%)	1 – 7	6
[$SnCl_2$], [$NaBH_4$] (%)	1 – 5	2
Liquid flow rate (mL min^{-1})	1 – 3	1.5
Gas flow rate (mL min^{-1})	100 – 350	325

Table 3

Variable	**Range investigated**	**Optimum value**
[HNO_3] (%)	1 – 3	1
Flow rate (mL min^{-1})	1 – 3	1
Probe position (cm)	0 – 2	0
Duty cycle (s)	0.1 – 0.5	0.5
Amplitude (%)	10 – 50	50
Extraction time (min)	1 – 25	25
Extraction volume (mL)	1 – 2	2

Table 4

	As	Hg	Ba
Precision (n=5) %RSD	12.7 (10 ng g^{-1}) 2.7 (100 ng g^{-1})	4.6 (10 ng g^{-1}) 3.6 (100 ng g^{-1})	4.2 (34ng mL^{-1})
LoD (ng g^{-1})	1.25	0.01	25
LoQ (ng g^{-1})	6.25	0.05	125
Calibration curve (R^2)	y=2.9121x+29.134 (0.9932)	y=1.3981x+175.75 (0.9938)	y = 0.005x - 0.0014 (0.9921)
Recovery (%)	91 (2.33 µg g^{-1})	93 (1.85 µg g^{-1})	87 (1.40 µg g^{-1})

Table 5

Paper	Hg (µg g^{-1})	RSD (%)	As (µg g^{-1})	RSD (%)	Ba (µg g^{-1})	RSD (%)
28·131·2095	0.150	22.8	8.623	12.1	1.093	23.7
28·131·20956	0.115	71.7	6.434	9.4	1.680	42.8
V·2008·2-991	0.011	37.1	0.069	78.6	0.659	14.8
V·2008·4-1486	1.097	57.3	0.775	27.5	0.528	13.4