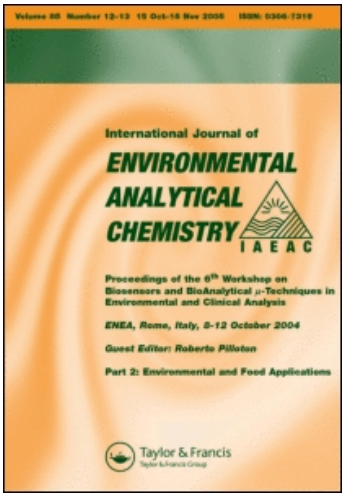

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Direct Determination of Cadmium in Blood and Urine by Zeeman Effect Electrothermal AAS

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Direct Determination of Cadmium in Blood and Urine by Zeeman Effect Electrothermal AAS*

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Cadmium in blood and urine was determined using a Stabilised Temperature Platform Furnace (STPF) without matrix modification or addition of an ashing agent. Calibration was done using dilute acid standards whose concentrations had been confirmed against diluted NBS-SRM Trace Elements in Water. The procedure was validated with samples obtained from exposed workers and supplied by the Inter-laboratory Comparison Program of the Toxicology Centre of Quebec, Canada.

KEY WORDS: Cadmium, blood, urine, electrothermal atomization, AAS.

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INTRODUCTION

Continuing interest in the effects of low-level exposure by cadmium and its compounds on human health has prompted the development and testing of analytical procedures for determining minute amounts of cadmium in biological tissues and physiological fluids. Progress in our understanding of the pathways of cadmium in humans depends on simple, accurate and rapid analytical methods. Electrothermal atomization AAS is an attractive instrumental technique because of its high sensitivity for cadmium and its relative simplicity and ready availability compared with electrochemical, neutron activation or emission spectrometric techniques.

The major drawback of ETA-AAS for the analysis of blood and urine arises from the large amounts of organic matter and salt which if not removed generates molecular absorption and light scatter, which greatly increase the background absorbance and impair the precision and accuracy of the determination. Thus, matrix modification procedures and pre-treatment of whole blood and urine samples are usually required (e.g. Refs. 1–11). In this paper we describe the validation of a direct injection procedure for analysing cadmium in these matrices without matrix modification or addition of an ashing agent. The advantage of such a procedure would be the virtual elimination of the reagent blank.

ANALYTICAL METHODOLOGY

Analyses were performed on an Hitachi Model Z-8000 Polarized Zeeman Effect AAS equipped with an autosampler, and using pyrolytically-coated graphite tubes and platforms supplied by Ringsdorf GmbH. An optical-temperature sensor was used for work with platforms to ensure maximum heating rate. The time-resolved absorbance signals were displayed on an integral CRT and printed out on the thermal printer of the instrument's computer. A Hamamatsu hollow cathode lamp was operated at 5 ma.

Cadmium standards were prepared by serial dilution of 1000 mg/l Spex standard (Spex Industries, Inc., Metuchen, N.J.) in 1% nitric acid (sub-boiling distilled from Seastar Chemicals, Sidney, B.C.) and subsequently stored in acid-cleaned polyethylene bottles. Distilled

water was passed through a Milli-Q system (Millipore Ltd., Mississauga, Ontario) before use.

Blood and urine samples were kindly provided by Dr. Jean-Philippe Weber of the Centre de Toxicologie du Québec (Université Laval, 2705 boul. Laurier, Québec G1V 4G2), as part of an Inter-laboratory Comparison Program. Whole blood was diluted 5 to 11 times with deionized-distilled water prior to injection into the graphite furnace. Initial experiments with whole blood were carried out on 5 times diluted samples. At this dilution and without the addition of Triton X-100, reproducibility of the analyte absorbances was occasionally less than satisfactory (greater than 15% RSD). In the final stages of development and for the assessment of the performance of the method, whole blood was diluted 1:10 with deionized-distilled water. Urine was injected without dilution.

New pyrolytically-coated tubes and platforms were conditioned as described previously,[12] except that atomization temperature was kept constant at the pre-selected value. For analysis, 20 μl aliquots were injected.

RESULTS

Optimum temperature program

The optimum temperature program for whole blood analysis is shown in Table 1. The drying program was selected by visually monitoring the sample drying process using a mirror supplied by the instrument's manufacturer, and a pen-light while observing the temperature on the video display to ensure that excessive boiling, bumping or splattering of the sample did not occur. Because we do not add Triton X-100 or other chemicals to prevent splattering, this was a critical step in the procedure.

Ashing temperatures between 300 and 1100 °C were investigated at an atomization temperature of 1800 °C. The decrease in absorbance between 400–500 °C relative to that measured at 300 °C (Table 2) indicates some loss of analyte which might be expected. However, the absorbances increased for ashing temperatures in the range 600 to 900 °C and thereafter decreased rapidly. A partial reason for this effect has been discussed previously.[12] It is also possible that analyte may be condensing at the ends of the tube and reappearing when the

Table 1 Temperature program for the determination of cadmium in whole blood and urine

Program step	*Temperature, °C*	*Time*
Dry	90–120	15 s
	120–150	30 s
	150–600	10 s
Ash	600–600	30 s
Atomization	2000–2000	7 s
Clean	2500–2500	3 s

Table 2 Effect of ashing temperature on absorbance signals at an atomization temperature of 1800 °C, $n = 5$

Ashing temperature	*Peak area absorbance (standard deviation)*
300 °C	0.0524 (0.0027)
400 °C	0.0368 (0.0024)
500 °C	0.0451 (0.0019)
600 °C	0.0531 (0.0009)
700 °C	0.0558 (0.0055)
800 °C	0.0669 (0.0081)
900 °C	0.0689 (0.0055)
1000 °C	0.0532 (0.0046)
1100 °C	0.0129 (0.0041)

temperature is raised during atomization. However, in order to test this suggestion it would be necessary to measure the tube temperature from the centre towards the graphite cones. The required 2-stage translation device coupled with an optical sensor is not available and so these measurements were not done to test this hypothesis.

The variation of integrated absorbance as a function of temperature was studied in the temperature range 1600 to 2300 °C. The results show that analyte absorbances were constant in the range 1800 to 2300 °C; relative standard deviation of the averaged atomic absorption signals in this temperature range was 2.6%. The average background absorbance was 0.1143 with a relative standard deviation of 5.2%.

Time-resolved absorbance profiles

Atom formation processes and vapour phase interferences can be investigated with the aid of time-resolved absorbance profiles. As one would expect the atomic absorption signals for a 1 μg/l cadmium standard in 1% nitric acid is clean and well-resolved from the practically non-existent background (Figure 1a). Using the temperature program listed in Table 1, a spiked seawater sample was studied (Figure 1b). The analyte signal is partially resolved from the very high background absorbance signal which peaks at ca 3 absorbance units. The overlap in the two signals occurs in an area where the background is less than 1.5 absorbance units and hence Zeeman correction can be expected to give an accurate result. Note that the

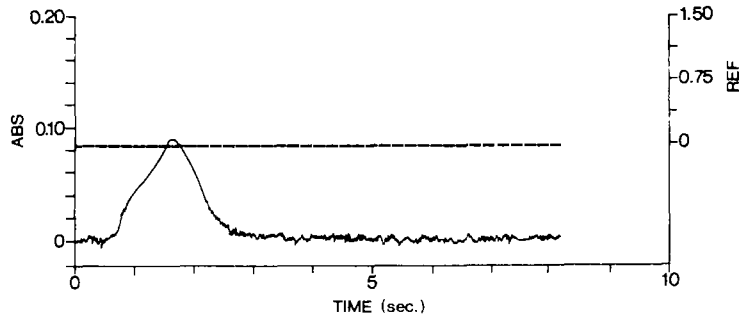

Figure 1a Absorbance–Time profile for Cd in 1% nitric acid.

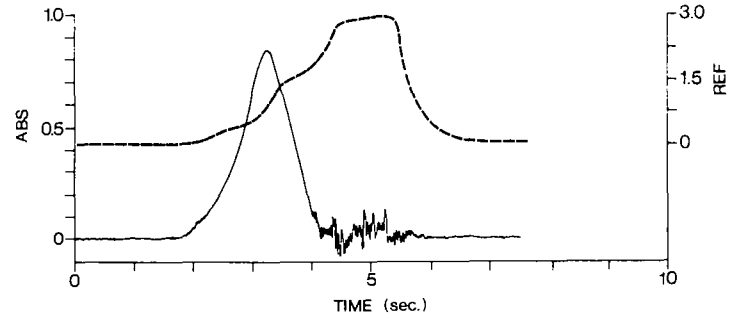

Figure 1b Absorbance–Time profile for Cd in seawater.

appearance time of the analyte is increased relative to the cadmium standard, suggesting that seawater contains substance(s) which decrease the rate at which atomization occurs. In the case of blood serum, the background absorbance signal shows the presence of two types of potentially interfering substances (Figure 1c). Partial overlap occurs only with the first of the two peaks and the background absorbance is well within the range where efficient correction can be achieved. The appearance time of cadmium in serum is identical to that for the cadmium standard. The profile for undiluted urine shows complete resolution of analyte and background absorbance signals (Figure 1d), although efficient correction of any direct overlap could be expected as neither of the two background peaks are over 1 absorbance unit. Cadmium in urine also has a similar appearance

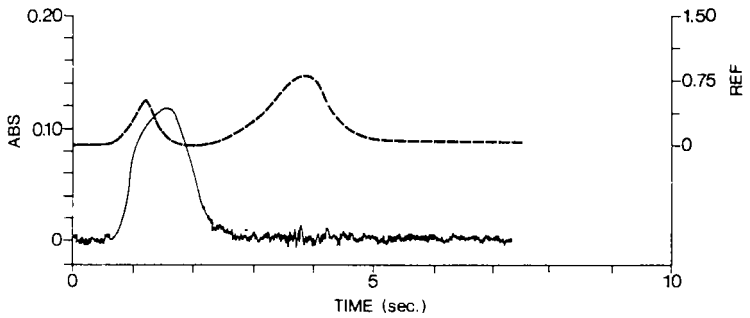

Figure 1c Absorbance–Time profile for Cd in serum.

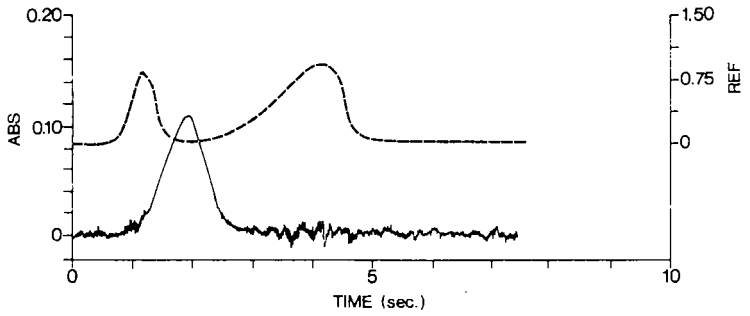

Figure 1d Absorbance–Time profile for Cd in urine.

time as cadmium in dilute nitric acid matrix. The last profile is for whole blood diluted 11 times with deionized distilled water (Figure 1e). The time scale shows the ashing stage and one can clearly see the very large (>1.5 AU) background signal during this step and the dramatic effect this has on the analyte signal. During atomization, however, the background doublet is not large especially in the region of overlap with the analyte signal.

Performance of the method

The procedure was validated by analysing six samples each of urine and blood (diluted × 11) obtained from exposed workers using the temperature program listed in Table 1. Each sample was loaded onto the autosampler carousel and interspersed with aqueous standards containing 1 μg/l of cadmium in 1% nitric acid. This standard had been checked for accuracy against diluted NBS-SRM 1643b Trace Elements in Water. Five replicate injections of samples and standards were run and the results are shown in Table 3. One of our main objectives here was to assess whether samples run in this fashion, without operator attention and monitoring tube performance with number of injections, would yield accurate results.

The results are generally well within 15% of the target concentrations (Table 3). Comparison with the target concentrations was done a year after the analyses were done when the Interlaboratory comparisons of the Centre de Toxicologie du Quebec for 1986 were

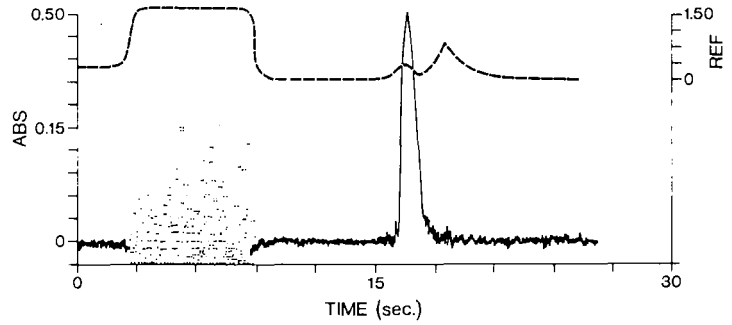

Figure 1e Absorbance–Time profile for Cd in blood.

Table 3 Cadmium in blood and urine provided by Centre de Toxicologie du Québec (concentrations in μg/l)

Sample	*Target concentration*	*This study (s.d.)*
Urine		
D-56	3.0	2.70 (0.07)
D-57	0.6	0.62 (0.05)
D-58	4.1	4.21 (0.06)
D-62	5.5	4.98 (0.06)
D-63	2.2	2.19 (0.17)
D-64	4.0	3.29 (0.02)
Blood		
C-73	1.5	1.50 (0.02)
C-74	4.5	3.50 (0.09)
C-75	6.0	6.20 (0.05)
C-79	5.0	4.70 (0.06)
C-80	9.0	8.08 (0.13)
C-81	7.0	5.40 (0.08)

made available. The target concentrations are set by elementary statistical analysis of the results reported by the laboratories (not including ours) participating in the Interlaboratory Comparison Program.[13] Usually the number of laboratories was greater than 16. The significant deviation of our result for C-81 from the assigned target concentration was likely caused by unusual behavior of this sample during the drying stage. In the development of the procedure we encountered one sample which did not dry completely following the general drying program and a modified program was established for this sample. This is of course not possible using an autosampler.

The detection limit of the method was calculated from the average absorbance values of the 1 μg/l standard throughout the development and testing of the procedure and the average blank absorbance value. These were 0.102 (s.d. = 0.015) and 0.0015 (s.d. = 0.0003) respectively. Taking twice the standard deviation of the blank value as the limit of detection gives a concentration of 0.006 μg/l.

CONCLUSIONS

The procedure described in this article offers a simple means of determining cadmium in whole blood and urine by direct injection

without the need for adding a matrix modifer or ashing agent. Calibration of the analysis is done using a dilute acid standard which had previously checked against diluted NBS-SRM Trace Elements in Water. The analysis of samples for exposed workers shows that the method yields accurate results. Variations in the constituents of blood samples can result in poor accuracy during unattended operation with an autosampler, because of loss of sample/analyte during the drying stage. This problem can easily be rectified by modifying the drying program accordingly.

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