

The Direct Determination of Cadmium in Blood by Electrothermal Atomization with the Graphite Platform

Application Note

Atomic Absorption

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Introduction

Recent developments in electrothermal atomization have facilitated the determination of trace metals in blood, even at such low concentration levels as those of the unexposed population [1-2].

From the analytical point of view, the blood matrix tends to produce perturbations during the atomization step due to the presence of significant concentrations of proteins and mineral salts. The proteins, which are not completely destroyed during the ashing step, produce a high background signal which often cannot be corrected.

This paper illustrates that deuterium arc background correction is satisfactory for the determination of trace elements in blood. Non spectral interferences produced by the abundance of mineral salts present in blood have been the subject of a number of investigations. In practice these may be reduced by the use of the graphite platform positioned inside the pyrolytic tube [3]. This publication illustrates this technique.



Agilent Technologies

Experimental

Apparatus

Agilent AA-1275BD Spectrophotometer

Agilent GTA-95 Graphite Furnace with Programmable Sample Dispenser.

Reagents

For dilution of blood Triton X-100 pro analysis Merck
0.2% solution

Matrix modifier HNO₃ Suprapur, Merck; diluted 1:1
distilled water

Results and Discussion

The following sequence was used: the GTA-95 autosampler automatically dispensed 2 µL nitric acid (50% v/v) and 3 µL distilled water, followed by the selected volume of blood.

Graphite Electrothermal Atomizer Conditions

Injection Temperature 150 °C

STEP NO	TEMP (°C)	TIME (SEC)	GAS FLOW (L/MIN)	GAS TYPE	READ COMMAND
1	550	60	3.0	air	
2	550	30	3.0	air	
3	550	5.0	3.0	argon	
4	550	2.0	0	argon	
5	550	2.0	0	argon	
5	1800	0.7	0	argon	*
6	1800	2.0	0	argon	*
7	2500	0.4	3.0	argon	
8	2500	2.0	3.0	argon	
9	150	11	3.0	argon	

The direct injection of the diluted blood into the graphite tube produced a very small and variable atomization signal together with an unacceptable level of background absorption.

The introduction of the sample on to the graphite platform produced an obvious improvement, but the injected volume cannot exceed 20 µL (10 µL blood 1:10 and 10 µL matrix modifier and/or water). Greater volumes lead to sample migration off the platform [4] as illustrated in Figure 1, column 1. This

limited volume leads to difficulties when determining cadmium at low concentrations. Indeed the blood of an unexposed population contains only 1-10 ng Cd mL⁻¹, and when diluted 10 times it may therefore be necessary to determine levels near 0.1 ng mL⁻¹ in extreme cases. For 10 µL diluted blood, this concentration represents an absolute mass of 1 pg cadmium which generates an absorbance signal of 0.015 in Peak Height [1]. Such a value is not really acceptable for analyses where good precision is wanted.

It was thus interesting to devise a method of injecting volumes greater than 20 µL on the platform so that low cadmium concentrations in blood could be measured with greater ease. To achieve this, the programmable injection temperature facility on the GTA-95 was used. In this case, the droplet is dispensed at 150 °C and partially dried without sputtering during this step. The dispensing of a volume of 20-25 µL blood (1:10) with 10 µL addition is then possible without risk of overflowing the platform and with good reproducibility. Under those conditions, the alignment of the injection capillary is not as critical as with injections at ambient temperature [4]. If the sample is dispensed on to a preheated platform, one must take care to observe the following rule: The blood aliquot in the capillary can never be preceded by an aliquot of nitric acid because this will cause an immediate and local coagulation of the proteins during injection and the capillary may then adhere to the platform. Consequently, as the capillary is moving out of the tube, the platform can also lift and then fall haphazardly as illustrated in Figure 1, column 2.

To overcome these problems, the blood aliquot must be separated from the acid aliquot by an aliquot of water. This is achieved by interchanging the blank and modifier vessels in the autosampler. Solutions are thus taken into the capillary in the sequence: acid, water, blood so that acid does not come into direct contact with blood until the time of injection on the platform.

The droplet form is then optimum and dispensing of 30-35 µL total volume is easily achievable. If the ashing step is performed in an argon atmosphere, the pyrolysis and matrix removal is not efficient enough. In this circumstance the background remains high, and the analyte signal is low and not reproducible (see Figure 1, column 3).

*More often than not, peak area measurements (integrated absorbance) are preferred. Whenever the matrix influences the speed of atomization of the analyte, measurements made in peak height necessarily vary with variations in the behaviour of the matrix while the integrated absorbance is hardly affected.

When analyzing low signals, near the limit of the method, experience shows that it is often more reasonable to use the peak height mode because the electronic noise will influence more directly the peak area during the whole integration time.

Air ashing considerably reduces the background level to 0.3 A for 20 μL blood (1:10), which is very easily corrected. At the same time, the analyte generates an acceptable signal (Figure 1, column 4, and Figure 2). To preserve tube life, a supplementary step (3) is used to flush argon for 5 seconds and eliminate the presence of air before atomization. Under these conditions, the platform life is very long, but carbon residue must be periodically removed by carefully scraping the platform.

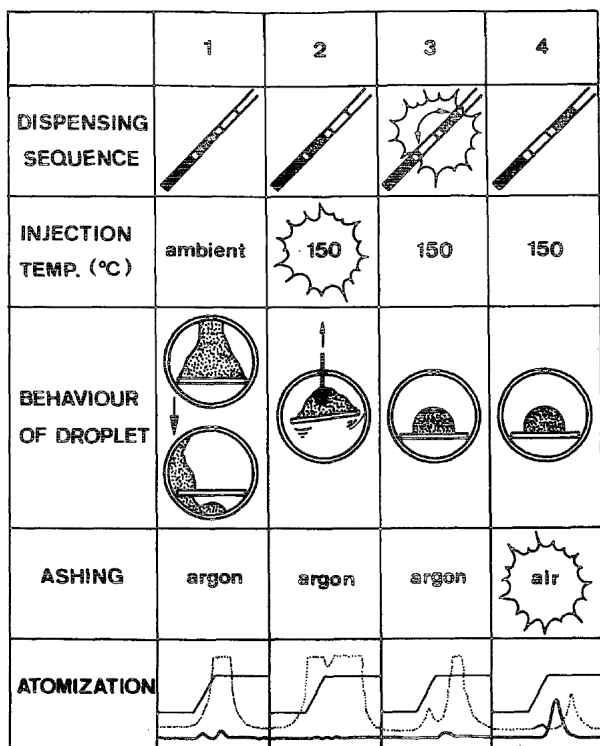


Figure 1.

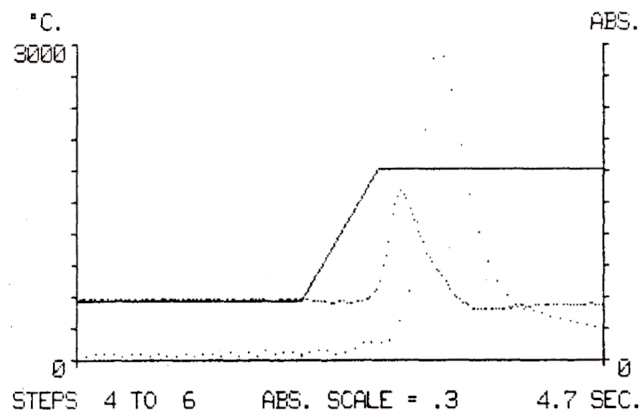


Figure 2.

This technique has been verified on several certified reference samples furnished by Behring Institute (Marburg — Germany) or Kardinske Institute (Stockholm, World Health Organization, United Nations, Environment Program). The measured cadmium concentration on the diluted blood samples (1:10) ranged from 0.05 to 3 ng mL^{-1} . The results are shown in Table 1.

No matrix effect was observed during the determinations and the standard calibration curve achieved with nitric acid is parallel to the standard addition curves obtained for blood.

The values shown in Table 1 were obtained by direct comparison with nitric acid standards.

Table 1. Determination of Cadmium in Blood

Sample	Value (certified) (ng/mL^{-1})	Value (found) (ng/mL^{-1})
Behring 131	0.5	0.7
Behring 132	6.5	6.8
Behring M-1	5.5	5.5
Behring M-2	30.0	31 *
Karolinska B	2.1	2.3
Karolinska N	10.5	10.7

Samples diluted with Triton X-100 (0.2%) 1:10
 Blood(1:10) = 20 μL
 (1:10) = 5 μL
 HNO_3 50% = 2 μL
 H_2O distilled = 3 μL

Conclusions

The method described here illustrates the possibilities of a modern electrothermal atomizer using the following improvements:

- Programmable sample dispenser
- Programmable injection temperature on a L'vov platform
- Automatic gas facility during ashing step

All these features permit easy determination of low cadmium concentrations in a matrix as difficult as blood, using a simple dilution without special additions.

The determination of other metals at low concentrations in blood would, in the same conditions, be as easy as cadmium. Indeed, as the relatively low ashing temperature efficiently removes the matrix in this example, the analysis of less volatile metals should not present major problems.

References

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