

A note on the sensitivity and accuracy of atomic absorption
spectrophotometry for trace metal measurements
on marine biological samples

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Summary

The results are presented of check experiments on the sensitivity and accuracy of atomic absorption spectrophotometry (AAS) which have been routinely applied to measurements of several trace metals in marine biological samples in the Monaco Laboratory. The results of these experiments show the importance of the application of a background corrector for accurate AAS measurements of cobalt and lead using a graphite furnace technique.

Résumé

Sont présentés ci-après les résultats des expériences de vérification portant sur la sensibilité et l'exactitude du procédé routinier de spectrophotométrie par absorption atomique (AAS) qui est appliqué par le laboratoire de Monaco aux mesures de plusieurs métaux à l'état de traces dans des échantillons biologiques marins. Les résultats de ces expériences révèlent l'importance de l'application d'un correcteur de bruits de fond aux mesures exactes faisant appel à la spectrophotométrie par absorption atomique et à l'utilisation de la technique du four à graphite pour le cobalt et le plomb.

During the course of 1974-76 the atomic absorption spectrophotometric technique (AAS) was used extensively in the Monaco Laboratory for measuring various trace elements in marine biological materials, in order to conduct homogeneity tests on the intercalibration samples for trace metals analysis as well as to obtain baseline data for trace elements on various kinds of marine organisms collected from different locations in the Mediterranean Sea. During this work sensitivity of the techniques used were repeatedly checked for various elements and the accuracy of the analyses were always critically

evaluated by analyzing standard reference materials. The results of these test experiments have brought to light critical points relevant to the application of AAS to routine analysis.

A Perkin-Elmer atomic absorption spectrometer Model 403 was used for the measurements in conjunction with either a three-slot burner for the flame work or with a graphite furnace for the hot flameless work. A deuterium arc background corrector was applied to some measurements by the graphite furnace technique.

Sensitivity of AAS: In order to determine running sensitivity of measurements attainable by our system for various trace elements of interest, the measurements were repeated by injecting standardized solutions of trace elements in appropriate concentrations into the system. The sensitivity of the measurements for the trace elements was expressed in terms of the concentrations of the elements, giving a reading of 1% absorbance for the flame technique or of the absolute quantities of the elements giving a similar reading for the graphite furnace technique. Average values of the sensitivity calculated from the results of the measurements are presented in Table 1. Although the sensitivity between two different techniques is not directly comparable, the sensitivity for the graphite furnace technique is given in the table in terms of the concentrations on the assumption that the same volume 10 μ l, was always used for each injection into the graphite furnace. By comparing the sensitivity between these two techniques, it can be roughly estimated that the graphite furnace technique increases the sensitivity by approximately two orders of magnitude for many of the trace elements listed. However, since the specific atomic absorption of solid samples in the graphite furnace technique is expected to be influenced by sample matrices involved, the sensitivity for some elements on real samples may be much lower than that given in the table.

Background correction in graphite furnace technique: Broad-band non-specific background absorption and/or scattering of the light caused by spattering and fuming of materials in the destruction of sample matrices or by evaporation of solvent, pose serious interference in the AAS, especially in solid source atomization, such as that using a graphite furnace. In order to compensate optically for this unwanted absorption or scattering, a technique using a continuous background spectrum, generated by a hydrogen

or deuterium arc source, has been developed and elaborated to adapt it to various optical systems [1-3]. In order to verify our measurements of cobalt and lead made by using flame techniques on the oyster homogenate sample MA-M-1, which was distributed for the intercalibration of trace element measurements, a series of measurements were carried out on the same sample by using a graphite furnace technique with or without the deuterium background corrector (DBC). The results of these measurements are summarized in Table 2. The results on the NBS's orchard leaf sample are also included in the table. As can be seen from the table, the results obtained by the graphite furnace technique without the DBC, are consistently higher than those with the DBC for both cobalt and lead, and the difference may reach more than one order of magnitude in many cases. It seems that the flame technique produces comparable results with those by the graphite furnace technique with the DBC, when the lead content of samples is significantly high or the matrix of samples allows it to attain higher sensitivity for cobalt.

Based on these observations, it should be emphasized that for some trace elements, the use of a deuterium background corrector is essential to obtain reliable results by atomic absorption spectrophotometry using the graphite furnace technique.

REFERENCES

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Table 1. Sensitivity of flame technique and graphite furnace technique in atomic absorption spectrophotometry for various trace elements

Element	Flame Technique	Graphite Furnace Technique	
	Sensitivity (ng/ml)	(ng)	(ng/ml)
Cr	100	0.02	2
Mn	60	0.008	0.8
Fe	150	0.06	6
Co	150	0.08	8
Ni	150	0.09	9
Cu	90	0.01	1
Zn	20	0.002	0.2
Ag	100	0.006	0.6
Cd	40	0.008	0.8
Pb	500	0.04	4

Table 2. Determination of cobalt and lead in the IAEA oyster sample, MA-M-1, and the NBS orchard leaf sample by various atomic absorption techniques.

Sample	Technique used	Co found ($\mu\text{g/g-dry}$)	Pb found ($\mu\text{g/g-dry}$)
Oyster homogenate MA-M-1	Flame	-	5.8 ± 0.8
	Graphite furnace without DBC [*]	7 ± 2	8.1 ± 0.6
	Graphite furnace with DBC [*]	0.38 ± 0.03	0.61 ± 0.04
NBS Orchard Leaf	Flame	0.25	44
	Graphite furnace without DBC [*]	5.2 ± 0.2	67 ± 6
	Graphite furnace with DBC [*]	0.21 ± 0.01	43.4 ± 0.7
	Certified value by NBS ^{**}	0.2	45 ± 3

* Deuterium arc background corrector

** U.S. National Bureau of Standards

DISCUSSION

Question and comment:

1. What is the theoretical value for Oyster homogenate MA-M-1 (Co and Pb)? (A. BALLESTER, Spain)
- There is no theoretical value for Co or Pb since the sample was not spiked. However, the results of the intercalibration show that the true values for Co and Pb are respectively close to 0,4 $\mu\text{gCo/g-dry}$ and 1.2 $\mu\text{gPb/g-dry}$.

