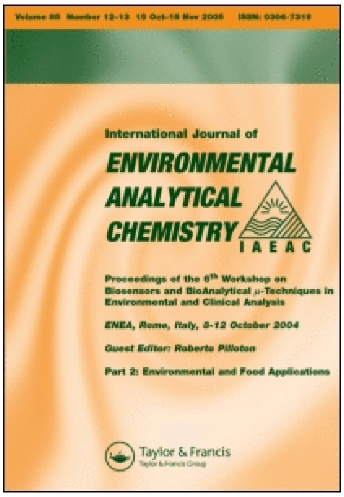

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The Determination of Metallic Elements in Wastes and Waters with the Graphite Furnace[†]

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The well-known technique of flame atomic absorption has the advantages of being easy to use, easy to interpret, and having good detection limits. It is unfortunate but true that the levels of metallic elements in many types of waters are easily high enough to be directly analyzed by the flame. However, in many other cases, better detectabilities are required. The HGA-2000 Graphite Furnace provides an improvement in detection limits up to 1000 times compared to the flame, and many samples can be analyzed with no pre-treatment. Natural waters are determined particularly easily by this technique; sea water, because of its high salt content and low trace metal content, presents more difficulty but can also be analyzed. The high sensitivity of the furnace also makes it suitable for the determination of metallic elements in air samples, because only a limited amount of air need be impinged for a measurement. Elements can be determined in some solids, such as hairs, and in oil spills to help identify the source.

INTRODUCTION

The technique for the determination of metallic elements by flame atomic absorption is now well known and well established. The method has many advantages, which need not be detailed here. However, like all analytical techniques, flame atomic absorption leaves room for certain improvements. Among the additional virtues that could be desired are greater analytical

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sensitivity and the ability to analyze solid samples without the need for prior dissolution.

Many devices have been used to increase the sensitivity of the atomic absorption method. The conventional burner is relatively wasteful of sample solution; therefore, Venghiattis,[1] among others, has developed burners with 'pre-heated' mixing chambers and increased the proportion of the sample which reaches the flame. The residence time of sample atoms in the optical beam has been increased by guiding the flame down a long tube.[2] A 'sampling boat', in which the sample is dried in a tantalum boat which is then placed into a flame,[3] has been used with some success for volatile elements, as has a more recent modification[4] in which the tantalum boat is replaced by a nickel cup. The recent emphasis on the determination of mercury has led to the development of a number of special-purpose cold-vapor devices, all of which are based more or less on the work of Hatch and Ott.[5] Specialized sample pre-treatment systems have been developed for arsenic and selenium.[6]

An effort to analyze solid samples directly was made by Venghiattis,[7] who mixed the powdered samples with gun powder and ignited the system in the sample beam of an atomic absorption instrument. His "SolidMix" sampling system had brief though spectacular life.

Several of these systems[3–6] are in commercial production and current use.

In the present work, attention will be confined to a general-purpose device, the Graphite Furnace, which has had its genesis in the work of L'vov,[8] Massmann,[9] and Woodriff and Stone.[10]

OPERATION OF THE GRAPHITE FURNACE

The principle of the Graphite Furnace is shown in Figure 1. A hollow graphite cylinder, approx. 50 mm long and 10 mm in diameter, is placed so that the sample beam passes through it. In the middle of the cylinder, at the top, there is a hole approx. 2 mm in diameter. Samples in solution, from less than 1 μl to 100 μl, are pipetted through the hole into the cylinder. Solid samples can be introduced through the open ends of the cylinder, after the hinged furnace assembly is tilted forward (Figure 2). An electric current is then passed through the cylinder walls in three stages. First a low current is used to dry the sample. Then an intermediate current is applied, which chars or ashes the sample. Finally, a high current is applied, causing the cylinder to be heated to incandescence and the sample to be atomized.

The cylinder is protected from oxidation by a constant flow of an inert gas, most commonly nitrogen. The hollow metal jacket surrounding the cylinder is water-cooled. A given amount of sample gives a much higher absorption in the furnace than it would in a burner. There are two reasons for the

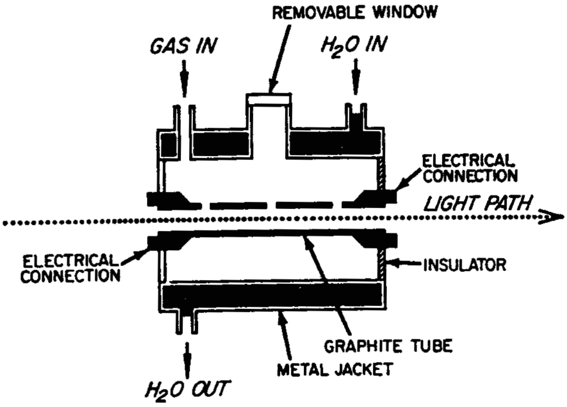

FIGURE 1 Simplified cross-section of Graphite Furnace.

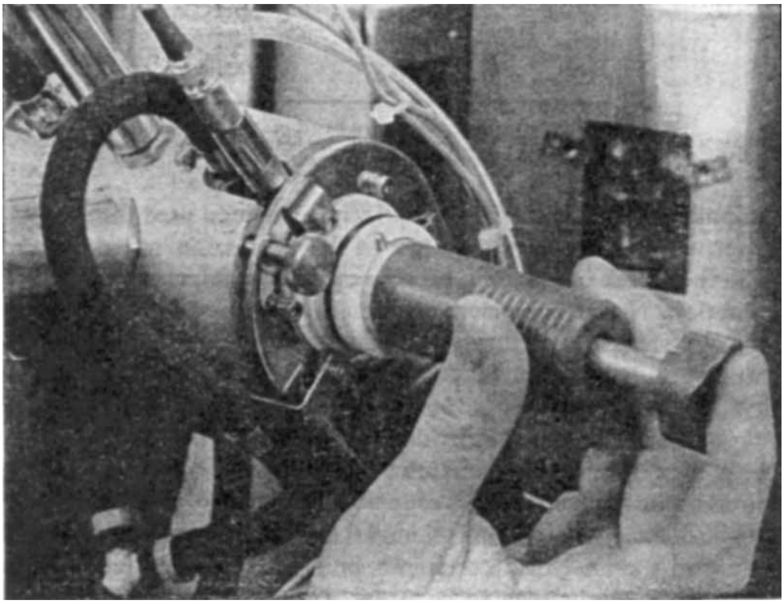

FIGURE 2 Solid sample is introduced into end of furnace.

difference. In a burner, a large proportion of the sample flows down the drain, while the furnace is nearly 100% efficient. Also, the sample atoms remain in the furnace for one second or more, whereas in the burner they leave the optical path in a small fraction of a second. As a result, the Graphite Furnace can determine most metallic elements 1000 times better than a conventional flame (Table I).

TABLE I

Comparative detection limits[a]

Element	Flame (μg/ml)	HGA-2000 Graphite Furnace (μg/ml)
Aluminum	0.02	0.00003
Cadmium	0.0002	0.000001
Chromium	0.003	0.00005
Cobalt	0.01	0.00004
Copper	0.001	0.00001
Gold	0.01	0.00008
Iron	0.005	0.00003
Lead	0.01	0.00006
Nickel	0.002	0.0001
Silicon	0.02	0.00008
Silver	0.002	0.0000025
Zinc	0.001	0.0000006

[a] Furnace detection limits are based on 100-μl sample. Flame limits were obtained with Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer.

Equipment based on the furnace principle has been used for several years. However, until quite recently the use of flameless sampling was regarded as being in the nature of research, because of various difficulties attendant upon its operation. Newer equipment now makes such operations more routine. A control system for the furnace, which incorporates a considerable degree of automation, appears in Figure 3. The drying, charring, and atomization currents follow each other automatically, at the touch of a single button. The proper currents for an individual analysis are set by the operator, with the help of a meter scale calibrated directly in furnace temperature. The durations of the individual stages are also under the operator's control.

A typical analysis, for chromium in aqueous solutions, is carried out according to the analytical conditions in Table II. The total analysis time for the sample can be seen to be 50 sec. Upon completion of the analysis, the tube takes no more than 30 sec to cool down in preparation for the next

FIGURE 3 Control system for Perkin-Elmer HGA-2000 Graphite Furnace.

TABLE II

Determination of chromium

	Temperature (°C)	Time (sec)
Dry	150	30
Char	1000	10
Atomize	2700	8

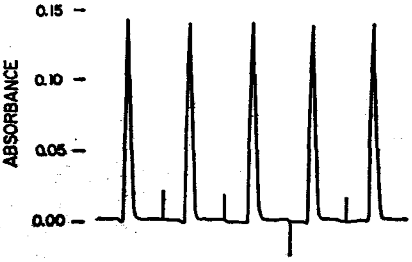

FIGURE 4 Replicate determinations of 20 μg/l chromium in water.

sample. It is therefore easily possible to analyze 30 samples per hour. Recorder tracings for the repetitive determination of 20 μg/l chromium appear in Figure 4. The sample size was 100 μl. The coefficient of variation is approx. 2%. Since the detection limit of atomic absorption for chromium is about 3 μg/l when a conventional burner is used, the advantage of a furnace for small sample concentrations is clearly illustrated.

It is possible to increase the sensitivity even further for some elements by arresting the flow of inert purge gas at the moment of atomization. If the purge gas is allowed to flow continuously, it has a tendency to sweep the sample out of the cylinder, thereby reducing the analytical sensitivity. It has been found that if the flow of purge gas is restarted within 10 sec of being cut off, no damage is sustained by the graphite cylinder. Figure 5 shows recorder tracings for aluminum with and without 'gas interrupt'. The improvement in sensitivity for this element is a factor of more than three.

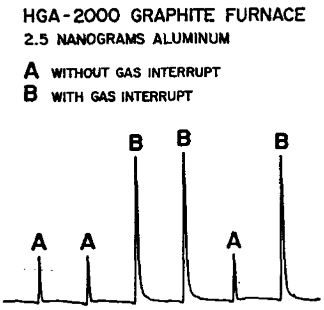

FIGURE 5 Determination of 2.5 ng of aluminum, A. without and B. with interrupted gas flow.

THE ANALYSIS OF FRESH WATER FOR POLLUTANT ELEMENTS

It is not considered difficult to analyze fresh waters for metallic elements by atomic absorption, even if the expected metallic concentrations are below instrumental detection limits. In general, a straightforward, non-specific extraction-concentration procedure is used.[11] A sample of perhaps 100 ml is acidified to the proper value, then shaken with a chelating agent and perhaps 10 ml of an organic solvent, such as methylisobutyl ketone. Most of the metallic elements go into the organic phase, yielding a ten-fold increase in concentration and leaving behind the alkali metals, alkaline earths, and most anions. Furthermore, the organic solvent itself yields about a three-fold improvement in analytical sensitivity. The total effect of the chemical procedure is therefore to improve the detectability of a given element by about 30 times.

Despite the simplicity of the chelating technique, it is clearly preferable to be able to analyze the sample directly without any sort of sample treatment. We analyzed the waters from a river flowing past our factory, as well as from a nearby lake, by both techniques, with the results shown in Table III. It is seen that the correlation is quite good.

TABLE III

Analysis of lake and river water

	Lake*		River*	
Element	HGA	Flame	HGA	Flame
Cr	1.8	2	2.2	2
Cu	0.7	1	0.4	1
Mn	2.7	3	1.3	1
Pb	1.8	2	2.7	3
Zn	0.6	0.8	1.0	1.2

*All concentrations in μg/l.

THE ANALYSIS OF SEA WATER

The analysis of sea water with the Graphite Furnace gives rise to some additional problems. The high concentration of NaCl can produce very great non-specific background absorption during the atomization stage, which will mask the much smaller absorption from the element of interest. Segar and Gonzalez[12] have done experiments concerning the previous volatilization of the salt matrix, but have found that the metals of interest are co-volatilized to a very great extent. They therefore used an extraction procedure similar to that discussed above, which leaves behind the sodium chloride matrix. The advantage of the Graphite Furnace for sea-water analysis is its ability to detect very low concentrations in relatively small samples (on the order of 10 ml), replacing the previous need to operate on very great sample quantities (one liter or more).

In this paper,[12] the authors note, that the smooth graphite cylinder (shown in Figure 1) makes it difficult to accommodate large quantities of an organic solvent because the low surface tension of the solution causes it to spread across the floor of the cylinder and run out the ends. They therefore back-extracted the elements of interest from the organic solvent into an aqueous medium.

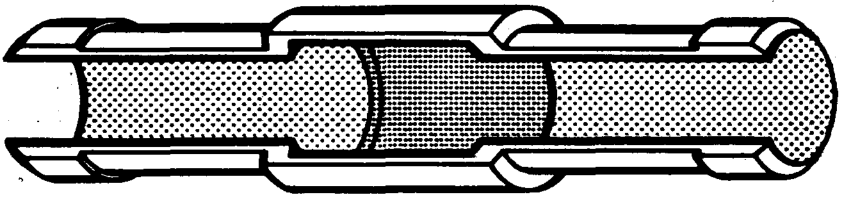

FIGURE 6 Cross-section of grooved graphite cylinder. Sample remains in center during drying and charring steps.

Of late, a different tube configuration has become available, with a shape as shown in the cross-section of Figure 6. This shape has two advantages: a more even distribution of temperature along the length of the tube, and the ability to retain the sample at the point when it is pipetted. With the new tube, it has been found that the back-extraction step is no longer necessary, and the organic solvents can be analyzed directly.

LEAD IN AIR

The determination of metallic particulates in air by atomic absorption is well known.[13] When very low concentrations are to be determined, one limitation of the conventional method is that a considerable volume of air must be impinged, requiring long sampling times. With the improved sensitivity available from the furnace, much shorter sampling times can be used. To analyze the air of Oslo, Norway, Omang[14] found it sufficient to aspirate air for only 10 min. He used a portable pump calibrated to 2–2.7 dm^3 air/min, collected on to 37-mm diameter MF-Millipore filters AA (0.8 micron), made of mixed cellulose esters. He soaked the filters in 2.0 ml of 1 + 1 nitric acid in a 50-ml beaker under gentle heat. After 5 min, the solution was decanted into a 10-ml volumetric flask, and the filters were washed with successive 2-ml portions of warm distilled water. Finally, distilled water was added to volume. The estimated detection limit was 0.2 μg lead per cubic meter.

THE ANALYSIS OF SOLID MATERIALS: LEAD IN HAIR

The analysis of hair for heavy metals has been of importance for many reasons. With the Graphite Furnace, it has recently been found possible to obtain detailed data on the exposure of human beings to lead by measuring the lead content of their hair one centimeter at a time.[15]

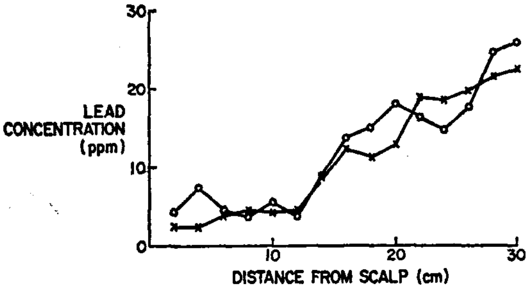

FIGURE 7 Lead concentration variation along the length of two different hairs from the same female head. Each data point in the figure represents a lead analysis on the preceding 1 cm section of hair.

Figure 7 shows the lead concentration variation along the length of two different hairs from the same female head. The authors conclude that lead has entered the hair by deposits on its surface, followed by diffusion into the hair. The hair was analyzed directly in the Graphite Furnace after being washed in diethyl ether in a Soxhlet apparatus.

Other materials, such as plastics and paper, can also be analyzed with little or no sample preparation.[16]

OIL SPILLS

Among the analytical techniques used to identify the sources of oil spills are the determination of the concentrations and ratios of various metallic elements in the oil, such as vanadium, nickel, chromium, iron, and copper.[17]

Very often, when a sufficient amount of sample is available, flame atomic absorption is sufficiently sensitive. The crude oil sample need only be diluted in an organic solvent such as MIBK to enable it to pass through the nebulizer capillary. When low levels are to be detected, or the available sample is limited, the use of the Graphite Furnace yields an improvement in sensitivity.[18]

BACKGROUND CORRECTION

Earlier in this paper, reference was made to non-specific background absorption. This occurs to a greater or lesser extent in many analyses performed with flameless sampling devices, where smoke or extraneous particulates produce absorption which is not caused by the element of interest. Moderate levels of background absorption can be removed by the use of an instrumental device called the Deuterium Background Corrector,[19] detailed discussion of which is beyond the scope of this article. When background correction is used, it is important that it occurs at the same analytical line as is used for the element of interest, that it occurs simultaneously with the analysis of the sample, and that the source of background radiation is as bright as possible, preferably a deuterium arc.

The use of background correction at a different wavelength, at a different time, or with a weak emission source, is likely to lead to analytical error.

THE PLACE OF THE BURNER

Despite the desirable qualities of the Graphite Furnace, the conventional atomic absorption burner retains sufficient advantages for many analyses and its use should be continued in most laboratories. With the burner, precision of about 0.3 % of the amount present can be achieved, compared to 1–5 % with the furnace. The burner should be used to analyze solutions where maximum sensitivity is not required or when sample volume is not limited, as the risk of sample contamination is less, speed is higher, and the burner is easier to use. Furthermore, the determination by the burner can be made directly in concentration on digits, whereas the Graphite Furnace requires measurement of peaks in a recorder. The Graphite Furnace therefore represents a powerful complement to a conventional premix burner, but not a replacement for it.

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