

Sampling Improvements in Atomic Absorption Spectroscopy¹

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ABSTRACT

Atomic absorption spectroscopy is being used as a routine method to determine sodium, potassium, calcium, magnesium, copper and many other metallic elements in oils, fats, milk and other substances. Copper and iron can be measured directly in milk without sample preparation. When highly acidified samples are run, a new plastic-lined nebulizer is useful to prevent spurious results due to corrosion. A new sampling device, the Graphite Furnace, can analyze extremely small samples and gives detection limits in the picogram (10^{-12} g) range.

INTRODUCTION

Atomic absorption is now a well established method for the analysis of edible oils, fats and fatty substances for metallic elements. A variety of sample preparation methods are used. However, there appears to have been remarkably little published on the routine analysis of these substances.

The method published by Guillaumin in 1966 (1) for the determination of calcium and magnesium at low levels in oils follows: Make up 1% solution of La in methyl alcohol and isoamyl acetate; make standards in this solution; dissolve 0.1 g to 3 g of sample in the lanthanum solution; and aspirate. Sample heating may be needed.

With certain hard fats, the sample solution must be heated to 40 C during aspiration to prevent them from solidifying in the nebulizer. The standard solutions are similarly heated in those instances.

Prevot has published a similar, though more complicated, method for the determination of sodium and potassium (2). The concentration levels of interest in his samples were extremely low and extractions were sometimes required. At the present day, given such a sample, we would be tempted to analyze it by flame emission without extraction. The detection limits for sodium and potassium by flame emission are at least 10 times lower than by atomic absorption. Most modern atomic absorption spectrophotometers are also capable of being used for flame

emission.

Recently, Brooks et al. have published a method for determining the major elements (sodium, potassium, calcium and magnesium) in milk (3). An outline of the method follows: add 50 ml of 24% trichloroacetic acid (TCA) to 5 ml of milk; shake and filter, dilute with La Solution; and run against aqueous standards.

The precipitation procedure is used to remove potentially interfering materials, primarily casein. Considerable time is saved in comparison with previous methods for determining these elements. However, the large dilution involved makes the determination of trace elements difficult.

DIRECT ANALYSIS OF MILK

Since modern burners and nebulizers can efficiently handle suspensions or solutions with a relatively high solids content, we decided to investigate the direct determination of copper and iron in milk. It is well known that high concentrations of copper in milk result in an unpalatable taste known as oxidized flavor. The copper content of normal milk is typically below $0.04 \mu\text{g/ml}$.

Figure 1 shows recorder tracings obtained for the direct determination of copper in an undiluted milk sample, at a wavelength of 3247 A. There are two potential interferences for this type of analysis, bulk or viscosity type interference, and background absorption.

Background absorption is a non specific signal from light scatter or absorption by molecular species and causes erroneously high results. We checked for background absorption by also analyzing the sample for silver at the 3281 A wavelength. Since one can be sure that the milk contained no measurable amount of silver, any reading obtained at this nearby wavelength could be attributed solely to background absorption. The background signal, equivalent to approximately $0.02 \mu\text{g/ml}$ copper, is subtracted from the copper absorption.

The sample was also run by the method of additions, to test the effect of bulk type interference. One milliliter of an aqueous $2 \mu\text{g/ml}$ copper standard was added to 99 ml of milk to give an added copper concentration of $0.02 \mu\text{g/ml}$, with negligible change in the physical characteristics of the sample. The results obtained, correcting for background absorption, were $0.022 \mu\text{g/ml}$ by comparison with aqueous standards, and $0.017 \mu\text{g/ml}$ by the method of additions. These results indicate that the direct analysis is satisfactory. The sample was also analyzed for iron, at a wavelength of 2483 A. The results are shown in Figure 2.

¹One of 28 papers presented at the Symposium, "Metal-Catalyzed Lipid Oxidation," ISF-AOCS World Congress, Chicago, September 1970.

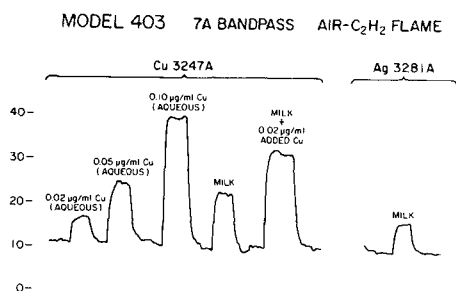


FIG. 1. Recorder tracings for copper in undiluted milk. The Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer was used with a three-slot burner head and an air acetylene flame. At the right, there is a tracing for silver in milk. This is attributed to background absorption.

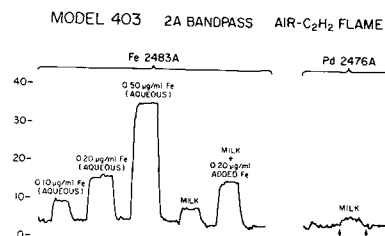


FIG. 2. Determination of iron in undiluted milk, directly and by additions. Background correction was made at the nearby line for palladium.

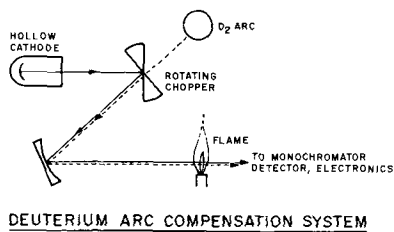


FIG. 3. Schematic diagram of the Deuterium Background Corrector.

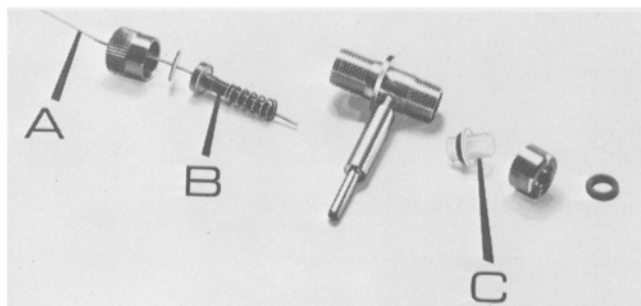


FIG. 4. Corrosion-resistant nebulizer—disassembled view. The capillary is made of Teflon, the venturi of Kel-F.

STAINLESS STEEL BURNER HEAD AND NEBULIZER
DETERMINATION OF Cr IN 30% AQUA REGIA

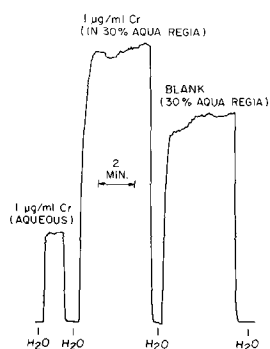


FIG. 5. Determination of chromium in aqua regia, with stainless steel nebulizer. Note corrosive effects of acid.

Background correction was made by analyzing the milk for palladium at the 2476 Å line. The milk was found to contain 0.08 µg/ml iron. The background was equivalent to only 0.02 µg/ml iron.

THE DEUTERIUM BACKGROUND CORRECTOR

The use of a nearby nonabsorbing wavelength to correct for background absorption is effective but time-consuming and dependent on the availability of appropriate nonabsorbing lines. A quicker and more general technique is the use of a Deuterium Background Corrector (4). The principle of this type of correction is shown schematically in Figure 3.

In the double-beam system, the beam from the hollow cathode lamp is passed alternately through the flame and past the flame. The beam that bypasses the flame is called the reference beam. When the background corrector is switched on, a deuterium arc lamp, which emits a continuum, is energized and the reference beam is interrupted. The rotating sector mirror now alternately passes the beam from the hollow cathode lamp and the beam from the deuterium arc through the flame. The element of interest absorbs only light from the hollow cathode lamp, but the background absorption is the same whether the deuterium

TITANIUM BURNER HEAD
CORROSION RESISTANT NEBULIZER
DETERMINATION OF Cr IN 30% AQUA REGIA

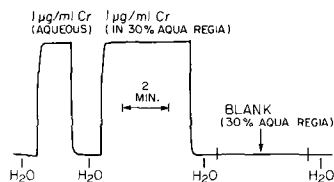


FIG. 6. Determination of chromium in aqua regia with corrosion-resistant nebulizer.

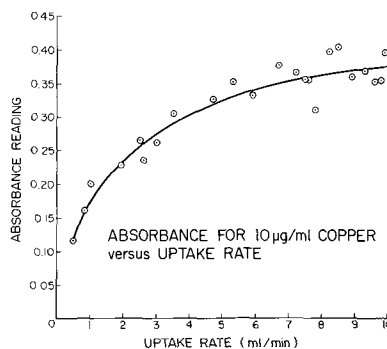


FIG. 7. Adjustable nebulizer; plot of absorbance vs. sample uptake rate.

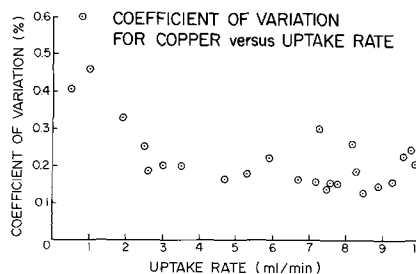


FIG. 8. Adjustable nebulizer: plot of precision vs. sample uptake rate for 5 µg/ml copper.

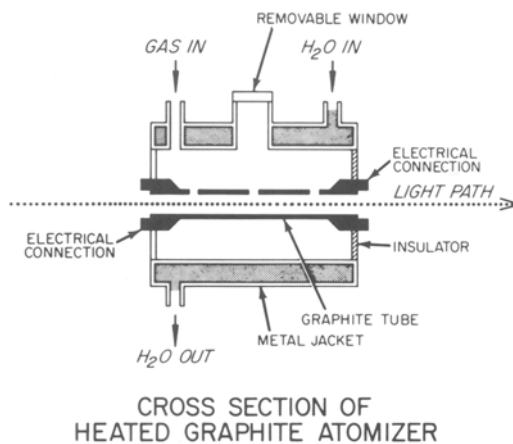


FIG. 9. Cross section of the heated graphite atomizer.

arc or the hollow cathode lamp is used. Therefore, the absorption of the background is cancelled.

CORROSION RESISTANT NEBULIZER

In 1964, J.B. Willis published an article on the determination of copper in butter, in which he extracted copper and iron from the butter by shaking the sample with nitric acid

TABLE I

Detection Limits of the Graphite Furnace for Typical Elements

Element ^a	Detection limit, g	Relative detection limit, $\mu\text{g}/\text{ml}^b$	Relative detection limit, flame, $\mu\text{g}/\text{ml}^c$
Silver	7×10^{-13}	0.000007	0.002
Aluminum	2×10^{-11}	0.0002	0.03
Arsenic	2×10^{-9}	0.02	0.1
Bismuth	5×10^{-11}	0.0005	0.04
Cadmium	2×10^{-13}	0.000002	0.001
Cobalt	2×10^{-11}	0.0002	0.01
Chromium	5×10^{-12}	0.00005	0.003
Copper	2×10^{-12}	0.00002	0.002
Iron	6×10^{-12}	0.00006	0.01
Iridium	4×10^{-10}	0.004	2.0
Manganese	2×10^{-12}	0.00002	0.002
Nickel	2×10^{-11}	0.0002	0.01
Lead	1.5×10^{-11}	0.00015	0.02
Selenium	1×10^{-9}	0.01	0.1
Thallium	5×10^{-11}	0.0005	0.03
Zinc	2×10^{-13}	0.000002	0.002

^aExamples only. About 60 elements can be determined with the graphite furnace.

^bBased on 100 μl iter sample.

^cMeasured with Perkin-Elmer Model 403 and appropriate fuel-oxidant combinations.

(5). Besides the relatively complicated sample preparation, Willis observed problems because the nitric acid leached copper and iron from the nebulizer that he was using, and gave him spuriously high results. The problem of acid attack of stainless steel nebulizers has continued ever since.

Recently, a corrosion resistant nebulizer has become available, in which the sample uptake capillary and the nebulizer capillary were made of one piece of Teflon (6). A disassembled picture of the nebulizer is shown in Figure 4.

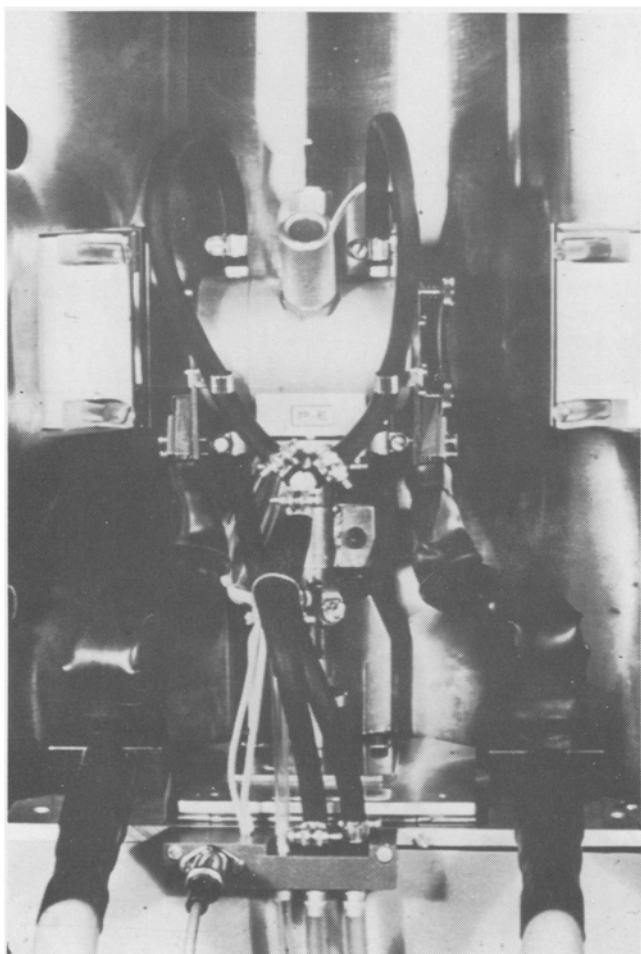


FIG. 10. Sample being pipetted into Graphite Furnace.

The only other part of the nebulizer which comes into contact with the sample is the venturi, which has been changed from stainless steel to Kel-F plastic.

The effectiveness of the nebulizer is shown in Figures 5 and 6. Figure 5 shows the use of a stainless steel nebulizer in the determination of chromium in aqua regia. From left to right are tracings for 1 ppm chromium in aqueous solution, then 1 ppm chromium in aqua regia, and then the aqua regia blank. It is apparent that chromium is being leached out of the nebulizer and the ragged tracings indicate that the nebulizer is also rapidly being destroyed by the acid mixture. Figure 6 shows the same analyses with the corrosion resistant nebulizer. It is apparent that the sensitivity from chromium in aqua regia is the same as that for water, and that the aqua regia blank has disappeared.

ADJUSTABLE UPTAKE RATE

The new nebulizer also has an adjustable uptake rate, which is of particular use when there is only a limited amount of sample available. For best absorption, the nebulizer is usually set to aspirate about 6 ml/min, but the uptake rate can be considerably reduced without commensurate losses in absorption.

Figure 7 gives a plot of absorbance versus sample uptake rate with the adjustable nebulizer. The best absorbance is at

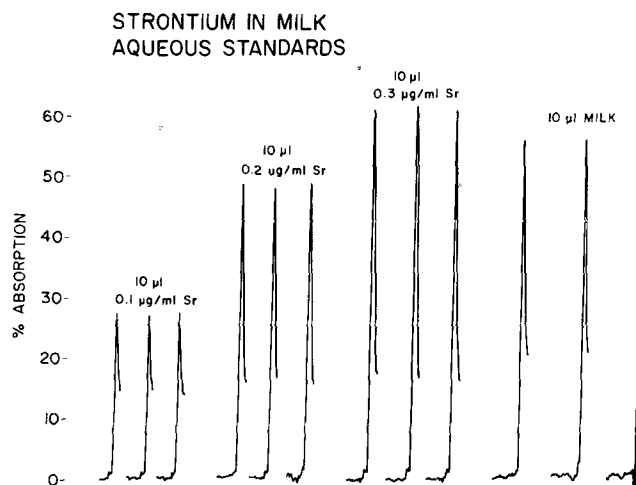


FIG. 11. Strontium in milk vs. aqueous standards. HGA-70 Furnace was used.

about 6 ml/min, but if the sample is scarce the uptake can be reduced to 1 ml/min with only about a 50% loss in absorbance. This is not only a more efficient use of samples, but also tends to minimize clogging in situations where this might be a problem.

At low rates of sample consumption, analytical repeatability continues to be good. Figure 8 gives a plot of coefficient of variation, as a function of nebulizer uptake rates. Down to levels as low as about 2 ml/min, the precision for 5 $\mu\text{g/ml}$ copper, determined with the Perkin-Elmer Model 403, remains at the favorable level of 0.2% of the amount present. After that, it tends to rise, but at 1 ml/min is still around 0.5%, which is by no means inadequate for most analyses.

THE GRAPHITE FURNACE

For extremely small amounts of sample and for extremely low levels of metallic elements an entirely new sampling system has become available which replaces the burner for these applications. This is the Graphite Furnace, offered under the tradename of HGA-70, or Heated Graphite Atomizer. The device, based on the work of the Russian physicist L'vov (7), as modified by the German physicist Massmann (8), is shown schematically in Figure 9.

A hollow graphite cylinder, about 1.0 cm in diameter and 5 cm in length, is placed in the optical beam of the atomic absorption spectrophotometer. The cylinder is open at both ends. The walls of the cylinder contain three small holes. The sample is introduced through the center hole, while the holes on both sides admit an inert gas, such as argon or nitrogen. The ends of the cylinder are connected to electrodes, which in turn are connected to an electrical power supply capable of passing as much as 500 amp at 10 v through the cylinder walls. The system is enclosed in a vaportight covering and is fitted with an inlet for the inert gas. The cover itself is water-cooled.

A typical analytical procedure is as follows. Up to 100 μl of the sample is pipetted into the cylinder. A low current is then passed through the cylinder walls in order to dry the sample. If ashing is required, this can be accomplished by using a somewhat higher current. It is generally possible to tell when the sample preparation is completed by observing the emission of smoke from the ends of the cylinder. The current is then raised to a high value, causing the cylinder walls to glow white hot. The sample is atomized rapidly and a tall narrow peak, generally less than 2 sec wide, is observed on a laboratory recorder. Since the sample is dried before it is atomized, the furnace technique reads out in weight rather than in concentration. Analytical levels are shown in Table I. It can be seen that typical levels are around 10^{-11} g, or 0.01 ng. It may be of some passing interest to note that these detectabilities are, in general, better than their counterparts by neutron activation.

A picture of the apparatus is seen in Figure 10. The device was tested for the determination of strontium in milk, both by the method of additions and against aqueous standards. Figure 11 shows some recorder tracings for the direct determination. Ten microliters of milk were used. The replicate tracings give an idea of the repeatability to be expected. Since the readings for milk fall midway between 0.2 and 0.3 ppm strontium, the milk appears to contain

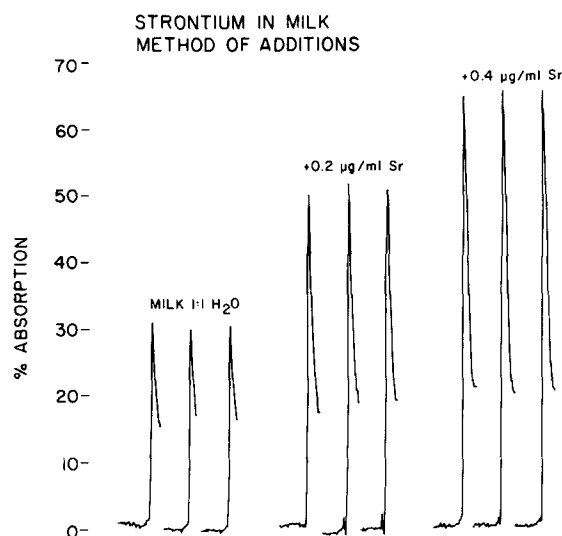


FIG. 12. Strontium in milk, method of additions.

0.25 ppm strontium.

Figure 12 shows the same analysis by the method of additions. Here, the tracing for the milk is just slightly higher than half the tracing for the addition of .2 ppm strontium. Therefore, it can be estimated that the value is again .25 ppm strontium. The method of additions is shown not to be required for this analysis, since the result agrees with the value obtained with aqueous standards.

It is interesting to note that in the additions work the milk was diluted with water. Since the sample is dried before it is atomized, the amount of aqueous dilution is immaterial; the only thing that matters is the volume of milk that was used. This is in direct contrast to work with a conventional burner nebulizer.

The Graphite Furnace is a very new device and analytical methods are only now being developed. There is no complete knowledge of its advantages and limitations, but enough is known to prove that the Graphite Furnace extends the domain of the atomic absorption spectroscopist into sample sizes and concentrations that have previously been beyond analysis. It will not, however, replace the burner for conventional analyses, because the burner is still much cheaper, much faster and very well proven. We like to think of the Graphite Furnace as an indication that the field of atomic absorption is by no means static and that a great deal of progress in many directions is still being made.

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