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Publication Date

1985-03-01

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für Analytische Chemie

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This work was supported by the Director's Office of Energy Research,
Office of Health and Environmental Research, U.S. Department of Energy
under Contract No. DE-AC03-76SF00098.

DIRECT ZAAS ANALYSIS OF SOLID SAMPLES: EARLY DEVELOPMENT

Tetsuo Hadeishi and Ralph McLaughlin

This paper presents the pioneering developmental work on direct detection of elements in a solid sample by Zeeman Atomic Absorption Spectroscopy (ZAAS) that took place from about 1971 to 1978 at the Lawrence Berkeley Laboratory. Our first task was the detection of mercury in food since this was a very important environmental problem in 1971 and still is. After demonstration of direct ZAAS detection of mercury in the period 1971-1972, this technique was extended to other elements. First commercialization of direct ZAAS began in about 1978. In addition to acting as an impetus to such commercialization, this pioneering work also stimulated development of the inverse ZAAS technique by others.

One of the most obvious methods for high sensitivity detection of trace elements in solid samples is simply conversion to the atomic vapor by heating and detection of the element of interest by atomic absorption. High sensitivity occurs since resonance absorption by atoms has a very large absorption cross section (the order of 10^{10} cm^2). However not all of the solid sample can be converted to atomic vapor which causes a severe background absorption problem resulting from molecules and particles that absorb and scatter incoming light. Direct ZAAS was developed to reject this severe background while allowing measurement of the element of interest.

In 1972 the first direct ZAA instrument was constructed and results of its operation were reported [1]. This was a very "clean" ZAA experiment because a single isotope was used (^{198}Hg) and single Zeeman components were well separated by a magnetic field of 7 kG (0.7T). The σ^+ and σ^- components of the Hg 236 nm line were isolated using a $1/4$ wave retardation plate and a linear polarizer. In this case the σ^- component is exactly at the peak of the Hg absorption profile while the σ^+ component is at the wing of the profile when it is broadened by a pressure of one atmosphere. Figure 1 shows the absorption profile obtained at one atmosphere by varying the magnetic field strength according to the Bitter magnetic scanning method [2] [3]. The experimental arrangement is shown in Figure 2. At 7 kG (0.7T) the wavelength separation between the σ^+ and σ^- components is 0.064 Å or 30 GHz while the line width of the Hg absorption at one atmosphere is about 6 GHz or 0.013 Å. This means the difference in absorption between the σ^+ and σ^- components is proportional to the concentration of Hg and if there is molecular absorption or particle scattering, the background effect on two wavelengths that differ by only 0.06 Å should be quite similar. Thus, the absorption difference due to the background is zero and only the Hg concentration will be detected if the difference in absorption between these components is recorded. Referring to Figure 2, it can be seen that rotating the $1/4$ wave plate passes the σ^+ and σ^- components periodically in time and these are detected by the photomultiplier tube. It can easily be shown that the difference in absorption is proportional to the density of the Hg vapor times the optical path length and the effect

of the background absorption or scattering is totally eliminated. Table 1 shows the experimental results for Hg determinations on various solid samples that only required about 10 seconds per analysis. These results are in excellent agreement with those obtained by other well established techniques. This was the first demonstration of ZAAS determinations of a trace element directly from a solid sample.

With the successful demonstration of ZAAS detection of mercury, it was obvious the the technique could be applied to other elements as well. The perpendicular Zeeman effect was utilized for this purpose in order to simplify the construction of light sources. Isotope mixtures that occur in nature were used in lamp construction. The detection scheme is quite similar. A typical arrangement is shown in Figure 3. A lamp placed in a magnetic field and observed in a direction perpendicular to the field exhibits a Zeeman pattern such that light polarized parallel to the field is either unshifted or only slightly shifted about the position of the zero field line. Light polarized perpendicular to the field direction is also shifted symmetrically on both sides of the line center but to a greater extent than that polarized parallel to the field. For this reason light polarized parallel to the field can be used to monitor the sum of atomic and background absorption (called π Zeeman components) while light polarized perpendicular to the field can be used to monitor predominately the background absorption (σ Zeeman components). Thus, the difference in absorption between light polarized parallel and perpendicular to the field direction is proportional to the concentration of the element to be determined and independent of the background absorption. The perpendicular and parallel components can be selected rapidly by means of an electrooptical device called a current controlled phase retardation plate [4] rather than the rotating polarizer used for the parallel Zeeman effect.

The next most important part of a ZAA instrument for direct solid sample analysis is the atomization furnace. In spite of the excellent background rejection capability of this technique, no signal can be detected if no light is transmitted. If only a small amount of light gets through, the signal to noise ratio will be reduced. Thus, it is essential that a furnace be designed that minimizes background absorption during the atomization process. In almost every case, the amount of sample is not the limiting factor since it is the ratio of trace element weight to sample weight (ppm or ppb) that is desired.

If the concentration is very low, it is advantageous to use as much sample as the instrument is capable of handling. Also, for a volatile element such as mercury, it is necessary to atomize the sample rapidly to prevent the element leaving so slowly that only a small number of atoms are in the absorption region at any one time and to destroy volatile compounds of the element (e.g. methyl mercury). Thus, conventional furnace techniques such as the standard drying, ashing and atomization cycle can not be used. A typical design suitable for mercury determinations is shown in Figure 2. Since mercury oxide dissociates into atomic mercury at relatively low temperatures (ca. 600 °C), an oxygen atmosphere was used to aid the combustion of the organic compounds. This resulted in a reduced background and allowed mercury to be determined in an organic matrix such as fish meat.

If low volatility elements are to be determined, the problem of solid analysis is not as severe since the refractory element is not vaporized until high temperatures are reached. This enables one to dry and ash the sample to eliminate much of the background before atomization. However, this is not always true for the sample may contain a volatile metal organic compound such as tetraethyl lead or tetramethyl lead. In this case, the sample must be heated to atomization temperature before reaching the absorption region. Conventional furnaces with open ended windows cannot achieve this mainly because the gas temperature in the furnace is much lower than the wall temperature and this allows the sample vapor to diffuse out of the curvette before reaching a high temperature.

Figure 4 displays various furnace designs that can be used to reach higher gas temperatures [5]. The designs in Figures 4a and 4b are essentially the same. The 4a design was found to be more efficient in heating the furnace gas to a higher temperature but if the sample chamber in 4b is packed with graphite granules to increase the high temperature surface area, the behavior of both designs is comparable. Although the experiment has not been conducted, a closed system design, like that shown in Figure 4c should be the best. In this configuration the sample is vaporized in a closed space and kept there to achieve complete dissociation. The piston first moves because of thermal expansion of the sample vapor and then can be further moved mechanically to allow the vapor to enter the optical absorption region.

In spite of all these precautions, the background absorption problem will never be eliminated because if the background is reduced, more sample will generally be added to increase the sensitivity. This means that there will always be a need for some type of Zeeman background correction.

Conclusion

Considerable improvements in ZAAS have occurred since our early demonstration in 1972; both in the direct and inverse ZAAS techniques. If solid samples are to be analyzed directly, furnace design is quite important. The direct ZAAS technique offers a maximum of flexibility for furnace design. Future progress in both direct and inverse development will most likely be in the direction of true simultaneous multi-element detection.

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Table I. Comparison of isotope-shifted Zeeman-effect technique to other conventional methods.

Sample source and identification	Lab where tested	Method used	Their results (ppm)	Our results in -10 sec (ppm)
National Bureau of Standards Reference 1571 (orchard leaves)	NBS	Spark source mass spectrometer, neutron activation, chemical analysis with atomic absorption	0.2	0.20 ± 0.04
National Marine Fisheries Service, Seattle, Washington				
Sample 614-1200 (fish protein concentrate)	NMFS	Wet chemistry	0.72	0.72 ± 0.05
Sample 628-0400 (fish protein concentrate)	NMFS	Wet chemistry	0.59	0.53 ± 0.01
Sample S-433 (wet cod)	Phoenix Mem. Gulf Atomic NMFS	Neutron activation Neutron activation FDA method (wet chem.)	0.49 0.48 0.48, 0.45, 0.58	0.45 ± 0.02
Sample S-430 (wet halibut)	Phoenix Mem. Gulf Atomic NMFS	Neutron activation Neutron activation FDA method (wet chem.)	0.12 0.13 0.10, 0.14, 0.09	
National Canners Association Aceton powder tuna (white meat)	NCA	Wet chemistry	2.48	2.08 ± 0.02
Univ. of California at Davis UCD Control mare liver	LBL LBL	X-ray fluorescence Neutron activation	12.0 ± 2.0 11.0, 14.0	10.0 ± 0.3

Figure 1. Absorption profile of natural mercury vapor (isotopic composition is that found in nature) along with the emission profile of the ^{198}Hg 236 nm line split by a magnetic field of 0.7 kG (0.7 T). The natural mercury absorption is pressure broadened by one atmosphere of nitrogen.

XBL 723-474

Figure 2. Experimental arrangement for the first direct ZAAS measurement of solid samples.

XBL 731-104A

Figure 3. Experimental ZAAS arrangement using the perpendicular effect.

XBL 787 - 1213

Figure 4. Furnace designs to achieve high gas temperatures.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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