

Silver Medal Lecture

The following is the Silver Medal lecture delivered by Dr. R. F. Browner, the tenth SAC Silver Medallist, at the Research and Development Topics in Analytical Chemistry Meeting of the Division, held on March 28th and 29th, 1983, at Loughborough University of Technology.

Sample Introduction in Atomic Spectroscopy: the Oldest Problem, the Newest Frontier

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Atomic spectroscopy is a highly successful instrumental technique. Modern optical design, coupled with sophisticated microprocessor data collection and data processing, provides current instruments with performance that was unattainable even a decade ago. However, the one area where surprisingly little has been accomplished is that of sample introduction. Both in atomic-absorption and in plasma-emission spectroscopy, no major advances have been made over systems that owe their origins to nebulizers developed in the early 19th century, by pioneers of flame spectroscopy. For example, one of the most commonly used nebulizers in ICP spectroscopy today, the concentric all-glass nebulizer, is almost identical in form to the nebulizer described by Gouy in 1879.¹ This is not to imply that sample introduction systems as currently used are not effective. On the contrary, especially with atomic-absorption systems, pneumatic nebulizers are both reliable, simple to operate and relatively inexpensive. With inductively coupled plasmas, on the other hand, nebulizers are somewhat less reliable, largely because of limitations imposed by the lower gas flows used with plasma sample injection.

Inevitably, the over-all success and sophistication of modern instruments focuses attention on the weakest link in the system, the sample introduction process. Here, quite clearly, serious inadequacies exist. By addressing the problems directly it should be possible to improve analytical performance significantly. One reason why this has not already been accomplished, except on a rather *ad hoc* empirical basis, is that until recently reliable techniques for characterizing the sample introduction process have not been available. The recent development of improved techniques for taking such measurements²⁻⁷ has opened the way for making systematic studies, which can relate the properties of sample introduction systems to the analytical performance of flame or plasma spectrometers. Now that it is possible to make such measurements, it becomes much simpler to determine what the appropriate properties of sample introduction to optimize analytical performance may be. The first part of this paper will describe the problems and will deal with aspects of both flame and plasma spectroscopy where substantial improvements in measurement capability are needed, which it is hoped to accomplish by improving sample introduction. The second part of this paper will attempt to define the objectives, by discussing current knowledge of the interaction of samples with flames and plasmas, and from there suggesting fruitful lines of approach to making the much needed advances in sample introduction procedures.

Identification of Sample Introduction Problems

Flame Atomic-absorption Spectroscopy (FAAS)

There are several sample introduction areas where major problems are currently experienced. With flame atomic-absorption spectroscopy, there are four major aspects.

Inefficiency of sample transport with liquid sample introduction

Most of the sample introduced to a flame system is sent to waste, and typical transport efficiencies (ϵ_n) range from 5–10%.³ (Transport efficiency is defined as the percentage of analyte mass reaching the atomizer, compared with the mass of analyte aspirated.) This is an undesirable state of affairs for two reasons. Firstly, precious sample is discarded, resulting in a minimum requirement of 0.5–1.0 ml of solution for a stable signal; secondly, because so much analyte is lost, the analytical signal is much lower than it would be if all of the sample was utilized efficiently.

Sample introduction interferences

Flame AAS is relatively free from interferences, especially spectral interferences. However, matrix-induced vaporization interferences (of the $\text{Ca}^{2+}/\text{PO}_4^{3-}$ type) may still present problems,

particularly in the air - acetylene flame, although the higher temperature of the nitrous oxide - acetylene flame is generally sufficient for their resolution. These interferences result from the formation in the flame of less volatile species than would otherwise be present when nebulising pure solution. Vaporization of the less volatile species is inhibited, resulting in a lower atom density and hence a reduced signal.

Detection limits

Flame AAS has inadequate detection limits for many applications. While the use of graphite furnace AAS may improve detection capabilities substantially, at the present state of development it may also cause more severe and less well defined interference problems.⁸

Linear range

A further problem with flame AAS is the rather limited linear range available, at least with conventional AAS instruments. This is one of the main limitations of flame AAS as a multi-element technique in comparison with ICP spectroscopy. Additionally, it adds a time-wasting factor when unknown samples must be diluted in order to fall within this limited working range. Such steps are particularly tedious when the element to be determined is present in unknown samples covering a wide concentration range.

Inductively Coupled Plasma (ICP) Emission Spectroscopy

Inductively coupled plasmas also suffer from sample introduction problems. Although some interferences may not be as severe as with atomic absorption, others may be more substantial. Many of the problems associated with plasma sample introduction are similar to those with flames, but there are some noticeable differences. With the ICP, matrix-induced vaporization interferences are generally less severe, whereas problems of nebulizer salt buildup and particulate induced blockage are often found.

Inefficiency of sample transport with liquid sample introduction

The transport efficiency with liquid sample introduction for plasmas is generally 5–10 times poorer than for flames. We have tested a wide variety of ICP nebulizers and spraychambers, and found ϵ_n values in the range 0.5–2.0%.^{3,5}

Sample introduction interferences

Matrix-induced vaporization interferences are a relatively minor problem with the ICP. However, a newly recognised category of sample introduction interference, aerosol ion redistribution (AIR), can cause problems in certain situations.⁹ This type of interference results from the actual mechanism of aerosol generation in the nebulizer. When low concentrations of certain cations (e.g., sodium or lithium at $<20 \mu\text{g ml}^{-1}$) are present with high concentrations of certain matrix species (e.g., calcium or magnesium at $>1000 \mu\text{g ml}^{-1}$), the ratio of elemental concentrations in the aerosol can differ from that in the original sample solution. Consequently, the analyte mass transport rate to the plasma is altered, and an interference results. Enhancements are generally observed, and may be as great as 100%.

Detection limits

Although the detection limits for many elements are lower with the ICP than with flame AAS, they are still inadequate for many direct determinations of great importance in environmental and biological systems. Furthermore, there have been no major improvements in detection limits in the last decade. There is clearly a strong need for improvement in this area.

Aerosol Characterization and Transport

In order to overcome the deficiencies of liquid sample introduction listed above, an alternative approach to current procedures is called for. Progress in this direction additionally requires a sound base of fundamental knowledge on aerosol transport mechanisms. The interactions taking place between aerosols and the flame or plasma atomizers must also be better understood. All this, of course, presupposes the ability to characterize aerosol properties, such as transport efficiency and drop size distribution, with considerable accuracy.

Transport efficiency and W -parameter

Transport efficiency (ϵ_n), as mentioned earlier, is simply the ratio of the mass of analyte reaching the flame or plasma to the mass of analyte aspirated, generally expressed as a percentage. The W -parameter is a mass transport term, and describes the mass of analyte reaching the plasma per second.⁷ If the drop size distribution of an aerosol produced by a typical pneumatic nebulizer is measured it turns out to be relatively broad, with a median diameter in region of 30 μm . Many of the drops can be as large as 80 μm . It is often found that these large drops create significant vaporization interference problems with flame atomic-absorption spectroscopy and so must be removed from the aerosol.

It is possible to divide the aerosol conceptually into two groups, based on drop size, with a dividing line designated by d_{max} .⁷ The value of d_{max} is the diameter of some hypothetical drop, the contribution of which to the net analytical signal is less than 10%. Drops with diameters less than d_{max} give rise to a useful analytical signal; drops with diameters greater than d_{max} do not. Drops with diameters smaller than d_{max} also contribute to a useful mass transport term, W_u , whereas drops with diameters larger than d_{max} make up the excess mass transport term W_e . It has been shown that the value of d_{max} can be as low as 4 μm , for pure aqueous calcium solutions. Clearly, drops with diameters much in excess of 4 μm contribute no useful signal for calcium, under typical analytical conditions. Furthermore, they may contribute significant interference problems.

There are two alternatives for increasing total mass transport of analyte to the atomizer. Either: more total aerosol, irrespective of drop diameter, is allowed to reach the atomizer; or, alternatively, more small-diameter aerosol particles are generated. This would allow a greater analyte mass transport to the atomizer, without any increase in drop size. Of course, the influence of the increased solvent mass loading must be taken into account. This can cause severe atomizer temperature reduction, especially for the ICP. Unfortunately, there are no easy means of generating the "ideal" very fine aerosol for sample introduction, while maintaining high W_u values.

Drop size and interferences

Flame AAS. As an indication of how effective aerosol drop size control can be in reducing interferences, it has recently proved possible to eliminate most vaporization interferences in flame AAS without unduly compromising the analytical conditions.¹⁰ This is accomplished by the removal of aerosol drops with diameters greater than approximately 4 μm . Table I summarizes the interferences quoted in the literature. By suitable control of aerosol drop size, it has proved possible to reduce all of these interferences to $\leq 5\%$. The penalty paid for this freedom from interference is a reduction in W_u , which leads to a net drop in analytical signal. In atomic absorption, therefore, there appears to be a choice between interference freedom on the one hand, and signal magnitude on the other.

TABLE I

VAPORIZATION INTERFERENCES REMOVED BY CONTROL OF AEROSOL DROP SIZE			
Air - C_2H_2 — Ca/ PO_4 Mg/Si	Mg/Al	Mg/Ti	
	Mn/Al	Fe/Si	Mn/Si
N_2O - C_2H_2 — Mg/Ti Al/V	Mg/Al	Mo/Al	Al/Ti
	Cr/Ti, V, Mn, W, Fe		Ni/Ti, V, Cr, Mn, Fe, Co

ICP emission spectroscopy. As discussed earlier, the transport efficiencies of ICP nebulizers and spraychambers are very low (typically 0.5–2.0%). The question therefore arises whether it is possible to increase the analyte mass transport term, W , without degrading either the analytical signal or the magnitude of interferences. The options are essentially the same as for atomic-absorption spectroscopy: either more total aerosol is allowed pass to the plasma, or more aerosol with smaller diameter drops must be produced. However, with plasmas, there is no information available on possible d_{max} values, as systematic experiments have not yet been carried out. One difficulty with making such measurements is the near impossibility of changing the analyte loading without simultaneously changing the solvent loading. Plasma signals are extremely sensitive to water loading.¹¹ Any increase in total aerosol reaching the plasma will generally be accompanied by a related increase in water loading. The additional solvent will lower the plasma temperature and reduce the emission signal.

This discussion leads to the fundamental question as to what the ideal aerosol characteristics for an inductively coupled plasma actually are? Properties of importance are drop size, analyte loading and solvent loading. The last factor further breaks down to a consideration of both aerosol and vapour loading. At the present time, we really have relatively little detailed information on truly "ideal" aerosol characteristics for the ICP. One of the serious difficulties facing systematic studies in this area is that it is almost impossible to vary one of these parameters separately. Usually all change simultaneously with any variation in the sample introduction process.

Conclusions

Currently we have a few answers to the problem of sample introduction for flames and plasmas, but much work remains to be carried out. Nevertheless, it has recently at least proved possible to focus attention on to those areas which give the greatest hope of leading to worthwhile advances in sample introduction procedures.

I acknowledge the major contributions made to this work by the many student, postdoctoral and visiting scientists who have participated in the research.

This material is based on work supported by the National Science Foundation under Grant No. CHE80-19947.

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