

A Convenient Sample Introduction System for ICP, ICP-MS, and AA

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Sample introduction has been a problem for analytical chemists for decades. In 1984, Richard Browner and Andrew Boorn went so far as to call sample introduction “The Achilles’ Heel of Atomic Spectroscopy.”¹ Since that time, a multitude of variations have been developed and commercialized to address some of the deficiencies. The most common form in which samples are introduced for analytical spectrometry is as an aerosol via pneumatic nebulization. The inherent inefficiency of the nebulizer–spray chamber combination has been investigated by numerous authors, and Barry Sharp presented a thorough examination of the problem in two papers in 1988—one on nebulizers and a second on spray chambers.^{2,3} Attempts to increase the mass-transfer efficiency of the sample introduction system resulted in a wide range of solutions such as ultrasonic nebulizers (USNs) and high-efficiency nebulizers.

At typical flow rates, sample introduction systems based on a nebulizer–spray chamber combination deliver poor transport efficiencies, typically between 1 and 3%. The optimum strategy for improving performance is to increase analyte transport efficiency. Ultrasonic nebulizers are said to improve delivery by an order of magnitude, and nebulizers that introduce the aerosol directly into the plasma approach 100% efficiency, albeit at greatly reduced flow rates. Although solid sample introduction techniques have been reported that involve laser ablation, direct insertion devices, powders, or

slurries, these methods appear to have limited application, since most samples are prepared in solution.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and ICP-MS are robust and established techniques for elemental analysis. These instruments are capable of providing the required sensitivities, detection limits, and linear dynamic ranges for the quantitative determination of the majority of elements required. There are exceptions. The elements of group 14–16 typically exhibit low sensitivities, due in part to their relatively high ionization potentials. An area that continues to receive much attention is vapor generation. Several elements of particular concern to both the environmental and metallurgical communities are the so-called hydride-forming elements (As, Sb, Bi, Ge, Sn, Pb, Se, Te, and Hg). The transformation of elements into volatile species has continued to elicit interest from both the academic community and the contract laboratory environment.

There are several advantages to introducing the sample as a volatile species, and this has prompted Nakahara to describe it as the ideal method for sample introduction.⁴ The principal advantage is the high transport efficiency that can be achieved. Le et al. showed that around 95% of arsenic is removed from solution when solutions of arsenic(III) react with borohydride.⁵ A second advantage is the possibility of separating the analyte from the

matrix. In order to optimize these advantages, especially the latter, proper design of the phase separator is essential. One major drawback is that the vessel in which the hydride generation took place has meant that applications of the technique were typically limited to either single elements determination, where the atomic absorption technique provides excellent results when combined with a quartz tube atomizer, or multi element techniques using the ICP.^{6,7} Contract laboratories are normally required to determine and report on a large number of elements for the majority of samples that are analyzed. This requirement dictates the use of a multi element technique based on either atomic emission or mass spectrometry in order to provide timely results.

The use of vapor generation as a means of sample introduction for ICP-AES dates back to the late 1970s. These early systems used atomic absorption (AA)-type batch systems for the generation of the volatile species. Thompson et al. developed a continuous system and proposed the possibility of simultaneous determination of the hydride-forming elements. It was also

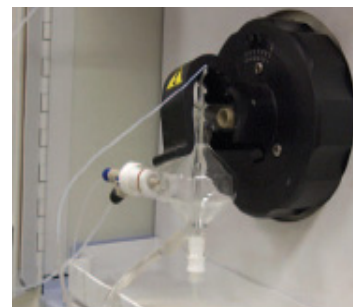
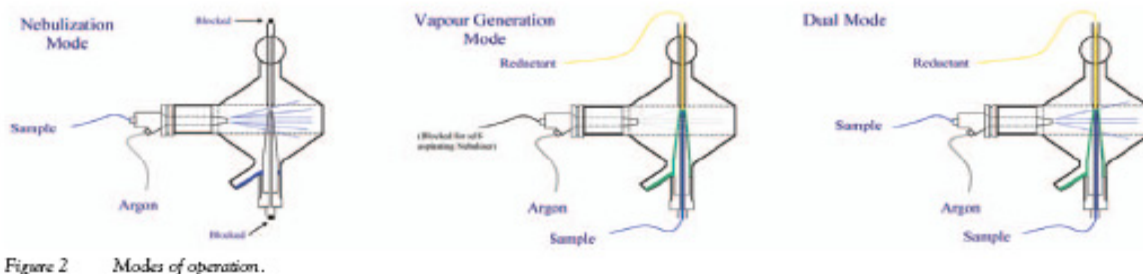


Figure 1 Multimode Sample Introduction System.



realized that the multi element capability of the ICP-AES could further be exploited through the simultaneous determination of conventional and hydride-forming elements. 8 Efforts over the last two and a half decades have provided a number of designs that seek to combine the nebulizing function with the vapor generation function into one device in order to determine, simultaneously, both hydride formers and non hydride formers. The first strategy used a dual tandem nebulizer design.⁹ A reductant solution aerosol, generated by the first nebulizer, was introduced into the gas orifice of the second nebulizer, to which the sample solution was fed. The mixed aerosol was subsequently introduced to the plasma. This approach, as well as other systems whereby the hydrides are formed using a nebulizer or “detuned” nebulizer, are non ideal, since a significant amount of reagent is introduced to the plasma.

A second strategy involved collecting the waste solution from the nebulized aerosol in a reservoir formed using an elevated drain inside the spray chamber.¹⁰ Here, the reductant solution was pumped into the reservoir to generate the hydride species. Hydrogen gas, which is also formed during the reaction, served to strip the volatile species from solution and into the spray chamber, where they become entrained in the sample aerosol that is transferred to the plasma. This basic approach has been used several times.

Reservoir-based systems have two primary disadvantages: sample crosstalk cannot be avoided, and high acid concentration is required to generate sufficient hydrogen for adequate stripping of the analyte. One system has a dedicated pump channel for the constant introduction of concentrated hydrochloric acid to ensure adequate hydrogen production. This extra channel allows the sample to be prepared at lower acid concentration, but issues remain in regard to the cost of the additional acid and to the safety of handling, the consequences of a highly corrosive environment, and the disposal of highly acidic wastes.

A third approach was to use a manifold system to mix the sample and reductant together in a T, after which the mixture is introduced into the spray chamber.¹¹ The drawbacks associated with this approach are described above.

A recurrent problem, and one that has challenged many researchers

over the last three decades, has been the rapid removal of the volatile hydrides (and other species) from solution. Early designs of the gas-liquid separator relied on high acid concentrations to strip the volatile species from solution, as described above. However, in a series of papers, Brindle and others showed that low acid concentrations resulted in better signals from hydride-forming elements, but they relied on a frit-based separator with argon flowing through it to generate small bubbles, thereby substituting argon for the chemically generated hydrogen to strip the volatile analytes from solution.¹² The importance of gas-liquid separator design on performance was further illustrated in a paper by Brindle and Zheng, who compared a variety of commercial and purpose-built gas-liquid separators for the determination of mercury by cold-vapor generation.¹³ The upshot was that the two designs that performed best were small dead-volume systems, designed for applications to flow-injection systems.

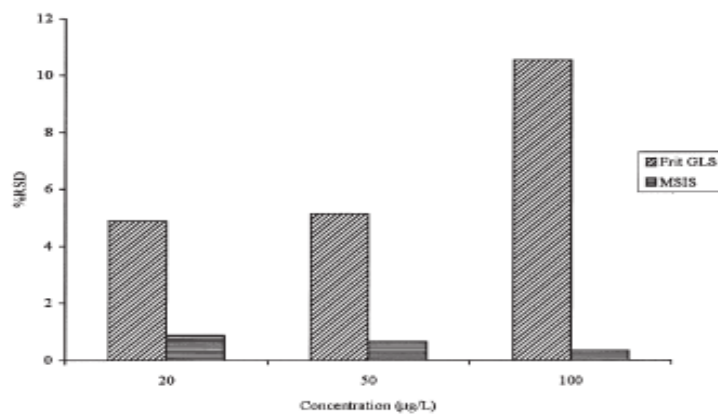


Figure 3 Comparison of %RSD for the MSIS versus a frit-based gas-liquid separator.

In 2002, McLaughlin and Brindle published a paper that presented a radically new design for the combined nebulizer/gas-liquid separator.¹⁴ The Multimode Sample Introduction System (MSIS) is based on a cyclonic spray chamber that has been modified by the addition of vertically opposed tubes in the center of the chamber (Figure 1). The device was patented in May 2005.¹⁵

The system is capable of operating as a conventional spray chamber, as a gas-liquid separator, or as both simultaneously. The various modes of operation are shown in Figure 2. The MSIS is unique in its approach to vapor generation in that it employs non-confined point gap mixing of the sample and reductant, and effective stripping of the volatile species using thin flowing film technology. The mixed solution in this case flows down a conical ground glass tube to the drain, where it is continuously pumped to waste. Gas from the nebulizer strips the volatile species and delivers them to the plasma. The sample flow can be split, delivering part of the solution for nebulization and the remainder for hydride generation. These characteristics virtually eliminate the possibility of sample cross-talk that is inherent with reservoir-based designs discussed above. The MSIS essentially eliminates signal noise caused by sputtering that occurs in manifold systems, where reductant and sample are mixed in a confined tube and where generated hydrogen inevitably results in bubble formation and pressure increases.

Detection limits for hydride-forming elements have values of 30 pg mL⁻¹ for arsenic (this work) and selenium. The MSIS, unlike frit-based gas-liquid separators, delivers performance similar to a conventional nebulizer-spray chamber in that the relative standard deviation (RSD) decreases with concentration. Frit-based gas-liquid separators, on the other hand, show

Table 1 Water pollution trace metals acceptance standards (dual mode) (lot #8040-04)

Element/line	Expected value (µg L ⁻¹)	Acceptance limits (µg L ⁻¹)	Experimental value (µg L ⁻¹) (n = 3)
Ag 328.068	181	155-208	169 ± 2
Al 394.401	1930	1580-2250	1850 ± 40
As 193.696	757	637-885	810 ± 30
Ba 233.527	1660	1440-1870	1640 ± 26
Be 313.042	164	138-185	172 ± 2
Cd 226.502	104	88.0-119	105.8 ± 0.4
Co 238.892	600	527-672	596 ± 10
Cr 267.716	903	788-1020	896 ± 14
Cu 327.393	375	319-431	359 ± 6
Fe 238.204	1890	1610-2170	1920 ± 30
Pb 220.353	1560	1370-1740	1561 ± 9
Mn 257.610	1610	1450-1790	1610 ± 20
Mo 202.031	59.2	44.6-73.2	49.7 ± 0.3
Ni 221.648	503	451-564	500 ± 2
Sb 206.836*	103	71.9-134	102 ± 2
Se 196.026	631	500-731	724 ± 4
V 309.310	569	467-671	554 ± 8
Zn 206.200	284	219-347	280.1 ± 0.9

*Trace metal standard lot #B20060194.

Table 2 Metals in sewage sludge CRM (dual mode)

Element/line	Expected value (mg/kg)	Prediction interval (mg/kg)	Experimental value (mg/kg) (n = 3)
As 193.696	6.45 ± 1.78	2.59-10.3	7.0 ± 2.0
Sb 206.836	38.4 ± 16.0	3.20-73.7	6.8 ± 0.9
Se 196.026	8.23 ± 2.46	2.92-3.5	7.9 ± 2.1
Al 394.401	21,700 ± 2460	16,300-27,200	23,300 ± 1600
Ba 230.425	906 ± 276	306-1510	545 ± 208
Be 234.861	88.3 ± 8.67	69.6-107	78 ± 8
Ca 317.933	45,900 ± 4900	35,000-56,800	45,168 ± 1900
Cd 226.502	5.74 ± 0.74	4.14-7.35	5.5 ± 0.2
Cr 267.716	37.2 ± 6.3	23.5-50.9	38.3 ± 0.9
Co 230.786	2.96 ± 0.67	1.46-4.43	2.3 ± 0.2
Cu 327.393	805 ± 91.1	609-1000	856 ± 43
Fe 238.204	9810 ± 824	7980-11,600	10,100 ± 820
Pb 220.353	119 ± 17.7	80.9-157	125 ± 10
Mg 279.077	4290 ± 407	3390-5200	4150 ± 230
Mn 257.610	199 ± 24.6	144-254	161 ± 5
Mo 204.597	11.4 ± 2.82	4.94-17.8	9.1 ± 1.2
Ni 232.003	19.6 ± 2.82	12.3-26.8	14.8 ± 0.4
K 766.490	2420 ± 295	1760-3090	2350 ± 190
Ag 328.068	101 ± 13.2	72.6-130	86.5 ± 19
Tl 190.801	85.9 ± 12.2	58.9-113	65.6 ± 6.4
V 290.880	114 ± 9.37	93.3-135	111 ± 11
Zn 206.200	1060 ± 86.6	861-1250	1088 ± 60

an alarming increase in RSDs as the concentration of analyte increases (Figure 3, adapted from Ref. 14). Furthermore, operation of the system for extended periods of time does not lead to the buildup of droplets in the injector and, in this respect, the device acts somewhat like a baffled cyclonic spray chamber.

Several features of the MSIS have attracted the interest of a number of laboratories. The Canadian Association for Environmental Analytical Laboratories (CAEAL) has approved its use for application to the determi-

nation of elements in sludges, biosolids, soils, drinking waters, and wastewaters. Benefits of the MSIS are 1) elimination of single-element technology (quartz furnace, for example) and 2) improvement in turnaround time for sample processing. Data for two different sample types, run on an Optima 4300DV (PerkinElmer, Shelton, CT) operating in axial viewing mode, have been presented here. The first sample type was a water pollution trace metals performance testing standard (Wibby Environmental, Golden, CO), and the second a metals in sewage

sludge certified reference material (CRM) (Resource Technology Corp., Laramie, WY).

Results and discussion

The results in *Tables 1* and *2* reveal the quality of data provided by the MSIS operating in a routine fashion using dual-mode operation (*Figure 4*). The Optima 4300 used relatively short (1–5 sec) instrument-selected integration times, indicating the type of performance that could be expected from an instrument operating in a typical contract or municipal laboratory. Results are almost uniformly of high quality; only in the sewage sludge standard reference material does the value for antimony vary significantly from the expected value (this discrepancy has been noted by others, who report values lower than the certificate), and the value for barium in the same sample exhibits unusually large standard deviation for reasons that are not clear.

Conclusion

The MSIS is a robust device for the determination of trace hydride-forming elements in a production laboratory. One of the authors (P. Cheese) has been using it on a routine basis for more than two years in the vapor-generation mode for the determination of As, Sb, and Se, where it has delivered satisfactory results in conformity with CAEAL requirements. For these elements, the required method detection limits could not be achieved using standard nebulization. Dual mode is not used in the particular case of the environmental laboratory since boron must be reported in samples. The MSIS, coupled with the ICP emission instrumentation, has enabled the laboratory to meet turnaround time requirements, illustrating how the MSIS delivers efficiency, as well as accuracy, for the routine environmental laboratory.

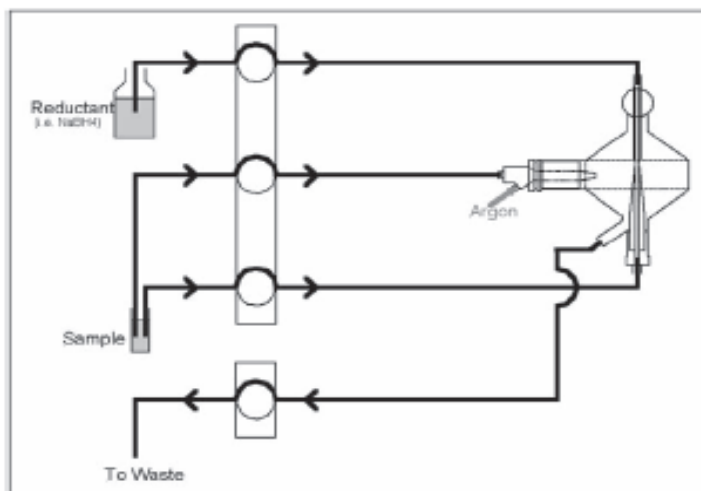


Figure 4 Dual-mode flow scheme.

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