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Simultaneous determination of hydride- and non-hydride-forming elements by inductively coupled plasma optical emission spectrometry

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This report surveys the historical development of dual-mode sample-introduction systems used with inductively coupled plasma optical emission spectrometry for the simultaneous determination of hydride- and non-hydride-forming elements by means of chemical hydride generation (HG) and pneumatic nebulization (PN), respectively. We highlight various aspects of this multi-element analysis approach, including the design of systems for simultaneous HG and PN, selection of (compromised) working conditions and their effect on analytical figures of merit, and applications to the analysis of real samples. We also highlight spectral and non-spectral interferences encountered during such operations.

Keywords: Analytical figure of merit; Dual-mode sample introduction; Hydride generation; Inductively coupled plasma optical emission spectrometry; Multi-element analysis; Non-spectral interference; Pneumatic nebulization; Simultaneous determination; Spectral interference

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1. Background

When Thompson and co-workers first combined the hydride generation (HG) reaction utilizing $NaBH_4$ (THB) with inductively coupled plasma optical emission spectrometry (ICP-OES) for elemental detection [1–3], the extremely efficient introduction of As, Bi, Ge, Pb, Sb, Se, Sn and Te into the plasma led to a significant increase in response for these elements. Aquo-ions of these elements were capable of forming stable covalent hydrides in the acidic medium by reduction with THB. As a result, limits of detection (LODs) for sample introduction with HG could be better than those obtained with conventional pneumatic nebulization (PN). Also, separation of the analytes from the sample matrix served to alleviate potential spectral interferences.

Although a real breakthrough in measurements of this limited group of elements had occurred, it appeared that use of the conventional U-type gas-liquid phase separator (Fig. 1) precluded concurrent simultaneous determination of the accompanying non-hydride-forming elements [4]. For this reason, from the start, several approaches were proposed to overcome this limitation and make possible multi-element determinations by ICP-OES equipped with a single universal sample-introduction interface capable of operating as both a conventional spray chamber for PN and a gas-liquid phase separator for HG, or simultaneously working in both modes, if desired.

One of the earliest approaches to such multi-element determinations of the hydride- and non-hydride-forming elements was a commercially available hydride generator from Nippon Jarrell-Ash (the

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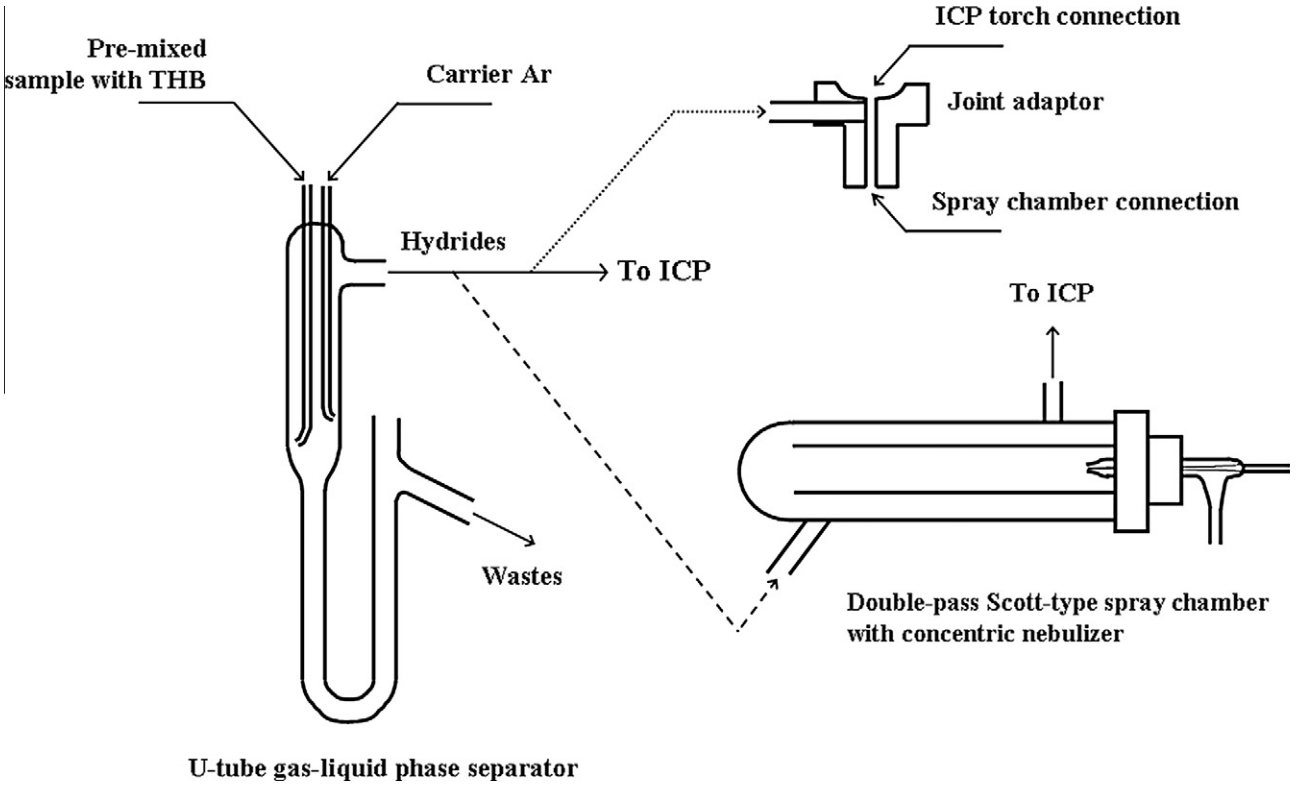

Figure 1. Integrated nebulizer/ hydride generator.

HYD-1), which was an automated mixing coil, double-stripping-type system similar to that described by Thompson. In this system, the volatile hydrides were continuously generated by reaction with THB and phase separated in a U-type gas-liquid phase separator. The gaseous reaction products were subsequently introduced into the plasma in a stream of Ar carrier gas through the drain outlet of a conventional spray chamber (Fig. 1). Although this arrangement was used for the determination of the hydride-forming elements only {i.e. As [5], Bi [6], Pb [7], Sb [8] and Se [9]}, it was feasible to change sample-introduction modes from HG to PN and *vice versa* without incurring adverse effects on the running plasma.

In a similar manner, another commercial U-type gas-liquid phase separator, the PS Analytical Automatic Hydride Generator (commercialized by PS Analytical), was also used. During operation, the volatile hydrides evolved in the HG reaction were separated in the U-type gas-liquid phase separator and introduced to the plasma *via* a specially-designed ball-joint adapter placed between the spray chamber and the plasma torch [10,11]. Using this interface, volatile hydrides could be transferred to the ICP without extinguishing the plasma and disconnecting the spray chamber (Fig. 1). Although simultaneous introduction of samples by means of both HG and PN was possible, it was only used for the determination of As, Bi, Sb, Se and Te following HG.

2. Nebulizer/spray chamber hydride-generation systems

Much closer to the objective of simultaneous determination of hydride- and non-hydride-forming elements by means of ICP-OES was use of sample-introduction interfaces based on unmodified or detuned pneumatic nebulizers fitted to conventional double-pass Scott-type spray chambers [11–27]. The HG reaction was commonly performed external to the spray chamber in T-pieces, Y-fittings, mixing disks or other types of junctions. The HG reaction occurred instantly, after merging the streams of acidified sample and alkaline THB solutions at these confluence points. The resulting reaction mixture, which included the evolved gaseous products and the post-reaction solution, was immediately delivered to the spray chamber *via* cross-flow [11,12,14–16,18], concentric [13] or dual Pt grid [17] nebulizers in order to complete the HG reaction and separate the volatile hydrides from the solution. This arrangement is depicted in Fig. 2. In this manner, these nebulizers also served as gas-liquid phase separators, facilitating efficient release of the entrained gases. The volatile hydrides, H_2 and the residual sample aerosol were swept by the Ar carrier gas from the spray chambers into the plasma and waste was removed continuously in the conventional manner.