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Abstract: The literature about direct solid sampling (SS) and slurry sampling atomic absorption spectrometry (AAS) over the past decade has been surveyed critically. It became apparent that a very significant change had occurred, particularly in the relation between the two major techniques used for that purpose. In the 1990s, slurry sampling was typically considered the technique of choice, combining the significant advantages of the solid and the liquid sampling methods, at least in part because of the availability of a commercial accessory for automatic slurry sampling. The situation is completely inverted now, as the above accessory has been discontinued and rugged and reliable accessories for direct SS became available. Direct SS electrothermal (ET) AAS has been shown to provide the best limits of detection because of the absence of any dilution and a minimal risk of contamination. Calibration against aqueous standards appears to be feasible after careful program optimization. The absence of any significant sample handling makes SS ET AAS ideally suited for fast screening analyses. The introduction of high-resolution continuum source AAS appears to open additional attractive features for SS ET AAS because of the significantly simplified optimization of furnace programs and the visibility of the spectral environment, which makes it easy to avoid spectral interferences. New calibration
strategies make a “dilution” of samples unnecessary, which used to be one of the major limitations of SS ET AAS. Finally, direct SS analysis is an important contribution to clean chemistry, as practically no reagents are used.

**Keywords:** Solid sampling, slurry sampling, electrothermal atomic absorption spectrometry, high-resolution continuum source atomic absorption spectrometry, clean chemistry

**INTRODUCTION**

The atomic absorption spectrometry (AAS), as it has been proposed for chemical analysis by Walsh in 1955 (1) was intended for solution analysis, using a pneumatic nebulizer; a spray chamber, where the sample aerosol was mixed with the oxidant and fuel gas; and a laminar flame for atomization. The use of solutions for chemical analysis undoubtedly has a number of distinct advantages. Solutions are easy to handle with conventional laboratory equipment, they can readily be diluted to bring the analyte concentration within the optimum working range, and the addition of buffers, releasers, and other reagents is straightforward. The introduction of solutions into all kinds of atomizers can easily be automated, and to bring a sample into solution is obviously the most efficient way of homogenization, resulting in excellent repeatability and precision. However, sample preparation for solution analysis is usually labor intensive and time consuming, and it is the major source of errors (2), mostly due to analyte loss and/or contamination. Sample digestion might also include health hazards for the laboratory personnel, and it usually produces a lot of corrosive and/or toxic waste. Last but not least, any digestion or dissolution is inevitably associated with a dilution of the analyte content, making solution analysis not necessarily suitable for determination of the lowest trace concentrations. Direct solid sample analysis has therefore always been investigated as an alternative in order to avoid the above limitations.

Two of the three sample introduction and atomization techniques routinely used in AAS, i.e., the flame technique and chemical vapor generation (CVG) are not particularly suited for solid sample analysis for different reasons. Conventional nebulizers can handle suspended solids only in exceptional cases without a high risk of clogging, and the flames used in AAS are only capable of vaporizing extremely small particles, as the time available for atomization is of the order of a few milliseconds, and the temperatures are only between 2250 and 2700°C. The few successful attempts for the analysis of slurries (3–5) or the direct analysis of solid samples (6–9) using flame atomization require specially designed accessories that are not commercially available, limiting these approaches to research.

The application of slurry sampling has been tried for both CVG AAS techniques, the cold vapor (CV) generation of mercury (10, 11) and hydride generation (HG) AAS (12–14), and more recently also with inductively
coupled plasma optical emission spectrometric (ICP OES) and mass spectrometric (ICP-MS) detection (15–19). However, at least for mercury, it has been shown that complete extraction of the analyte into the liquid phase is a prerequisite for CV AAS from slurries; i.e., this cannot really be considered solid sample analysis. An additional problem arises for HG AAS, as it is well known that for Group V elements (As, Sb, Bi) the oxidation state $+5$ reacts much slower and results in lower sensitivity than the oxidation state $+3$, and for the Group VI elements (Se, Te) only the oxidation state $+4$ is forming a hydride. In addition, most of the hydride forming elements are often present in biological and environmental materials as stable organic compounds, which do not form hydrides, and require harsh digestion conditions to be converted to the inorganic form. All this is obviously a source of error in slurry sampling CVG techniques, as no pre-reduction or harsh digestion is involved in solid sample analysis. These techniques will therefore no longer be considered here.

This means that there remains electrothermal (ET) AAS with graphite furnace (GF) atomization as the only technique to be considered for solid sample analysis with AAS. Direct solid sample analysis was actually the first application reported for ET AAS (20) back in 1957, when L’vov put a “pinch of NaCl” into a graphite furnace that was standing unused in a corner of his laboratory and watched how the radiation of a sodium lamp, passing through the furnace, disappeared upon heating the furnace. Solid sampling (SS) analysis has been used ever since in ET AAS (21), as graphite furnaces allow a relatively easy introduction of solid samples, and the atomization times are some three orders of magnitude longer than in typical flames, making possible complete vaporization and atomization of even relatively large amounts of sample. However, in spite of the obvious advantages of direct SS analysis, which are a significantly reduced sample preparation time and hence a faster analysis; higher accuracy, as errors due to analyte loss and/or contamination are dramatically reduced; higher sensitivity due to the absence of any dilution; and the absence of any corrosive or toxic waste, the method has not been really accepted until the end of the 20th century. The major arguments against direct SS analysis using ET AAS have been (a) the difficulty of handling and introducing the small sample mass, although a wide variety of tools has been developed for that purpose (22); (b) the difficulty of calibrating, which usually requires solid standards of similar composition and analyte content compared to the samples to be analyzed; (c) the limited linear working range of AAS and the difficulty of diluting solid samples; and (d) the high imprecision of the results due to the inhomogeneity of natural samples, which requires a large number of repetitive determinations. Slurry sampling ET AAS, in contrast to direct solid sampling, has been accepted much earlier as an alternative technique for sample introduction, mostly because of the availability of a commercial autosampler, the USS-100 (Perkin Elmer) for that technique (23). It therefore appears worthwhile to compare these two approaches regarding their pros and cons.
SLURRY VS. SOLID SAMPLING ET AAS

The book of Kurfürst (22) summarizes the literature about solid and slurry sampling up to the mid 90s, and Cal-Prieto et al. (24) published a review of the literature about slurry sampling for ET AAS from 1990 to 2000, so that only the most important aspects and recent development have to be considered here. The breakthrough of slurry sampling ET AAS clearly came with the introduction of the above-mentioned commercial equipment (23) that was based on extensive research work done by Miller-Ihli (25), and which consisted of a modified furnace autosampler, in which the slurries were homogenized by an ultrasonic probe immediately before their transfer to the graphite tube. In a review article about solid sampling in ET AAS, which covers the literature up to 1990, Bendicho and de Loos-Vollebregt (26) came to the conclusion that “the slurry technique gives better analytical performance than direct solid sampling”. This judgment was based on the facts that (a) the slurry concentration can be easily changed so that the analyte concentration falls into the analytically useful range of the calibration graph; (b) chemical modification is easier to perform in the slurry technique, because of more effective contact between the sample particles and the modifier, and (c) slurry introduction can be easily automated, hence combining the significant advantages of the solid and liquid sampling methods. This latter sentence has ever since been repeated in almost all publications about slurry sampling without considering potential progress in the field of SS that might relativize this statement.

One of the major problems of the slurry technique, which has already been recognized by Bendicho and de Loos-Vollebregt (26), is the stabilization of the slurries during the time until they are finally introduced into the graphite atomizer. Although various techniques have been proposed for homogenization of slurries, including the ultrasonic probe that is used in the USS-100, particle size distribution, specific gravity of the sample, sampling depth, and other factors were found to have an influence on the accuracy of the results (27). Several authors have been investigating problems associated with grinding time, particle size, and sedimentation errors (28–31), and a particle size $< 37 \mu m$ appears to be necessary to obtain accurate results, at least in the case of high-density materials. In contrast to sedimentation, flotage of light and finely ground material, such as biological samples or coal, on the surface has also been reported as a potential problem, which requires the addition of a surfactant, such as Triton X-100 (30).

Another very important factor in slurry analysis is the quantity of analyte that is extracted into the liquid phase, i.e., solubilized, during slurry preparation, which depends on the analyte, the matrix, the liquid phase, and the slurry preparation conditions, and which can be between 0 and 100% (32–34). Analytes are usually much more easily extracted from biological than from inorganic materials, and 100% extraction of Cd, Cu, Mn, and Pb has for example been reported using 1 mol L$^{-1}$ nitric acid and ultrasonic
agitation (35). Usually, a high extraction rate is considered advantageous, so that various authors have been using very high acid concentrations, including concentrated hydrofluoric acid for slurry preparation of environmental samples, such as fly ash, soil, and sediment (36–40), which obviously results in a similar corrosive waste problem as with conventional sample digestion. Cal-Prieto et al. (34) developed an analytical scheme for the determination of antimony in geological materials using slurry sampling ET AAS, an element, for which the extraction rate to the liquid phase was negligible. They found that the normalized absorbance remained constant up to a sample mass of 50 mg mL$^{-1}$, which corresponds to a sample mass of 1 mg in a 20-μL aliquot injected into the furnace. This corresponds to a typical sample mass used also for direct SS, as will be discussed later. Normally, however, significantly smaller sample aliquots are used for slurry sampling.

The same authors (34) also determined the minimum number of particles that should be introduced into the graphite tube in order to ensure the representativeness of the aliquot for the sample to be analyzed, and they concluded that a minimum of 50 particles have to be introduced. This determines the limits of the dilution that can be applied in order to determine higher analyte concentrations. This limit, similar to other problems such as sedimentation, obviously depends on the quantity of analyte extracted to the liquid phase, and disappears in the case of 100% extraction. Miller-Ihli (32) has therefore introduced the term “representative sample mass”, which takes analyte extraction into consideration. On the other hand, analyte extraction can also become a source of errors, as has been shown by Maia et al. (41) for the determination of Tl in marine sediment samples. Due to the presence of co-extracted chloride in the aqueous phase, extracted and added thallium was lost at pyrolysis temperatures above 400°C as volatile TlCl, whereas the non-extracted thallium was stable up to 900°C. Although the determination was made with ICP-MS in this case, the reactions in the graphite furnace are obviously independent of the detection system. This potentially different behavior of the analyte in the liquid and in the solid phase has to be taken into account as potential source of error particularly in cases where the analyte addition technique is used to correct for differences in sensitivity between the slurry and calibration solutions (34, 38). All these problems of sedimentation, extraction and distribution of the analyte between two phases are obviously non-existent in the case of direct SS analysis.

**DIRECT SOLID SAMPLING ANALYSIS USING LINE SOURCE ET AAS**

The situation regarding the commercial availability of equipment for slurry and direct SS has changed completely within the last decade. Firstly, there has been the ongoing effort of Krivan and co-workers at the Department of Analytical Chemistry and Maximum Purification at the University of Ulm,
Germany, to improve existing equipment for direct SS analysis (42, 43). The accessory he developed, which included a pair of tweezers for the reproducible introduction of a graphite platform containing the solid sample into the graphite tube has been further tested (44, 45) and introduced as a commercial device in the late 1990s. Nowadays, the second generation of this solid sampling accessory is available both in a rugged and inexpensive manual, as well as in a fully automatic version, as shown in Figures 1a and 1b. In the automatic version, the graphite platform with the solid sample is transferred first to an integrated micro-balance, and then into the graphite tube, and the software automatically calculates the integrated absorbance normalized for a sample mass of 1 mg. The second event was the discontinuation of the USS-100, the only commercially available autosampler for slurry sampling, which obviously completely inverted the situation comparing slurry and direct SS ET AAS, and also the conclusion, at which Bendicho and de Loos-Vollebregt (26) had arrived some 15 years ago. It is therefore time to reconsider the relation between the two approaches based on recent research and advances in that field.

Figure 1. Accessories for direct SS ET AAS; (a) manual system SSA 5, consisting of a pre-adjusted pair of tweezers for reproducible insertion of the SS platform; (b) SS autosampler SSA 62 for automatic transfer of up to 62 SS platforms to a microbalance and into the graphite furnace (by courtesy of Analytik Jena AG, Jena, Germany).

(continued)
Table 1 gives an overview over a number of representative publications in the field of direct SS ET AAS over the last decade, as the earlier literature is fully covered in the book of Kürfürst (22). The survey shows that a great number of elements have been determined in a wide variety of organic and inorganic matrices, including high-purity metals and metal oxides and plastic materials. Even natural waters have been analyzed, co-precipitating Cr with Pd/8-quinololonol/tannic acid (46) or As with Ni–ammonium pyrroli-dine dithiocarbamate complex (47), analyzing the precipitate directly in order to avoid dilution and potential errors in the dissolution step. One of the most important contributions in the field of direct SS analysis undoubtedly came from Krivan and co-workers (42, 43, 48–52) who showed in an impressive number of publications that SS ET AAS, at least in the analysis of high-purity materials, always gave the best limits of detection (LOD), even compared to much more sophisticated techniques, such as neutron activation analysis (NAA), ICP-MS, isotope dilution mass spectrometry (IDMS), and others.

The advantage of direct SS ET AAS is most obvious for materials that are very difficult to be brought into solution and for elements that are kind of omnipresent, and hence most susceptible to contamination. Friese and Krivan (43) determined seven trace elements in high-purity tantalum powders using a sample mass up to 60 mg and aqueous standards for
<table>
<thead>
<tr>
<th>Analyte</th>
<th>Matrix</th>
<th>Background correction</th>
<th>Calibration</th>
<th>Modifier</th>
<th>LOD&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi, Pb, Se, Te, Tl</td>
<td>Nickel-based alloys</td>
<td>Zeeman-effect</td>
<td>Aqueous standards</td>
<td>Ni</td>
<td>n.a.&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Single-alloy chips</td>
<td>(58)</td>
</tr>
<tr>
<td>Cr</td>
<td>Biological samples</td>
<td>n.a.</td>
<td>Addition calibration</td>
<td>None</td>
<td>n.a.</td>
<td>Comparison of calibration</td>
<td>(64)</td>
</tr>
<tr>
<td>Cu, K, Mg, Mn, Na, Zn</td>
<td>Molybdenum metal, molybdenum silicide</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>None</td>
<td>0.06–0.5 ng g&lt;sup&gt;−1&lt;/sup&gt; 0.5–4.5 ng g&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>Up to 80-mg sample introduced</td>
<td>(48)</td>
</tr>
<tr>
<td>Cd</td>
<td>Kidney, liver</td>
<td>Zeeman-effect</td>
<td>Aqueous standards</td>
<td>None</td>
<td>n.a.</td>
<td>Wet animal tissue</td>
<td>(62)</td>
</tr>
<tr>
<td>Cd, Cr, Mn, Pb</td>
<td>Biological samples</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>Pd (Cd only)</td>
<td>n.a.</td>
<td>Trace element distributions</td>
<td>(63)</td>
</tr>
<tr>
<td>Cu, Fe, Mn, Na, Zn</td>
<td>High-purity tantalum powder</td>
<td>Zeeman-effect</td>
<td>Aqueous standards</td>
<td>None</td>
<td>0.1–27 ng g&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>Up to 40-mg sample introduced</td>
<td>(42)</td>
</tr>
<tr>
<td>Cu, Fe, K, Mn, Na, Zn</td>
<td>High-purity tantalum powder</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>None</td>
<td>0.02–4 ng g&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>Transversely heated atomizer</td>
<td>(43)</td>
</tr>
<tr>
<td>Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Zn</td>
<td>High-purity tungsten</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>None</td>
<td>0.01–4 ng g&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>Up to 100-mg sample introduced</td>
<td>(49)</td>
</tr>
<tr>
<td>Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Zn</td>
<td>High-purity aluminium oxide</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>None</td>
<td>0.25–25 ng g&lt;sup&gt;−1&lt;/sup&gt;</td>
<td></td>
<td>(83)</td>
</tr>
<tr>
<td>Al, As, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sn, Zn</td>
<td>High-purity titanium</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>Carbon powder</td>
<td>0.02–30 ng g&lt;sup&gt;−1&lt;/sup&gt;</td>
<td>Single pieces of metal; up to 30-mg sample introduced</td>
<td>(50)</td>
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<tr>
<td>Sb</td>
<td>PVC</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>Pd</td>
<td>n.a.</td>
<td>Screening method</td>
<td>(59)</td>
</tr>
<tr>
<td>Element(s)</td>
<td>Matrix</td>
<td>Deuterium</td>
<td>Sampling Method</td>
<td>Standards</td>
<td>Acid</td>
<td>Modifier</td>
<td>Gas During Pyrolysis</td>
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<tr>
<td>As, Cd, Co, Cr, Ni, Pb, V</td>
<td>Barytes</td>
<td>Deuterium</td>
<td>Solid standards</td>
<td>HNO₃ (for Cr, Ni, V)</td>
<td>n.a.</td>
<td>Permanent modifier for solid sampling</td>
<td></td>
</tr>
<tr>
<td>Cd, Sn</td>
<td>Sewage sludge PVC</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>Pd or PO₄</td>
<td>n.a.</td>
<td></td>
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<tr>
<td>Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Zn</td>
<td>High-purity tungsten trioxide and tungsten blue oxide</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>H₂ gas during pyrolysis</td>
<td>0.07–2 ng g⁻¹</td>
<td>Coprecipitation with Pd/8-quinolinol/tannic acid</td>
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<tr>
<td>Cr</td>
<td>Natural waters</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>None</td>
<td>20 ng L⁻¹</td>
<td>Gas flow during atomization</td>
<td></td>
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<td>Cu, Pb</td>
<td>Sewage sludge</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>None</td>
<td>n.a.</td>
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<tr>
<td>P</td>
<td>Plastic materials</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>Pd + ascorbic acid</td>
<td>2.5 μg g⁻¹</td>
<td></td>
<td></td>
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<tr>
<td>Si</td>
<td>Niobium, titanium, zirconium oxides</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>CH₄ gas during pyrolysis</td>
<td>10 ng g⁻¹</td>
<td></td>
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<td>Cd, Cu, Pb</td>
<td>Mineral coal</td>
<td>Deuterium</td>
<td>Solid standards</td>
<td>Ru permanent</td>
<td>3–40 ng g⁻¹</td>
<td>Permanent modifier for solid sampling</td>
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<td>Tl</td>
<td>River and marine sediments</td>
<td>Zeeman-effect</td>
<td>Aqueous standards</td>
<td>Ru perm. + NH₄NO₃</td>
<td>20 ng g⁻¹</td>
<td>Permanent modifier for solid sampling</td>
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<td>Hg</td>
<td>Environmental materials</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>Pd permanent</td>
<td>200 ng g⁻¹</td>
<td>KMnO₄ added to stabilize Hg in aqueous solutions</td>
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<td>As</td>
<td>Sediment</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>None</td>
<td>440 ng g⁻¹</td>
<td>Residues from leaching processes</td>
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(continued)
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<tr>
<th>Analyte</th>
<th>Matrix</th>
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<th>Calibration</th>
<th>Modifier</th>
<th>LOD&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Remarks</th>
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<td>Fe</td>
<td>Rice plants</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>None</td>
<td>0.14 ng at 302.1 nm</td>
<td>Micro samples</td>
<td>(85)</td>
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<td>Co, Zn</td>
<td>Vitamin complex, agricultural soil</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>None</td>
<td>Co: 0.5 μg g&lt;sup&gt;-1&lt;/sup&gt; Zn: 4 μg g&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Gas flow during atomization 307.6 nm line for Zn</td>
<td>(55)</td>
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<td>As(III), As(V)</td>
<td>Sea water</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>None</td>
<td>20 ng L&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>Co-precipitation with Ni-PDC complex</td>
<td>(47)</td>
</tr>
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<td>Si</td>
<td>Polyamide</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>Pt</td>
<td>0.1 μg g&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>LOD better than with SS-ETV-ICP-MS</td>
<td>(75)</td>
</tr>
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<td>Cr</td>
<td>Milk powder, lobster hepatopancreas, polyethylene, sewage sludge</td>
<td>n.a.</td>
<td>Aqueous standards</td>
<td>None</td>
<td>2 ng g&lt;sup&gt;-1&lt;/sup&gt;</td>
<td></td>
<td>(86)</td>
</tr>
<tr>
<td>Mn</td>
<td>Vitamin-mineral tablets</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>None</td>
<td>n.a.</td>
<td>Comparison of calibration techniques</td>
<td>(65)</td>
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<td>Food samples</td>
<td>Deuterium</td>
<td>Aqueous standards</td>
<td>Pd + Ca</td>
<td>18 ng</td>
<td></td>
<td>(87)</td>
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<td>Cu, Zn</td>
<td>Bovine liver</td>
<td>Zeeman-effect</td>
<td>Aqueous standards</td>
<td>Zn: W + Rh Cu: 1.6 ng Zn: 1.3 ng</td>
<td>Cu: 216.5 nm Zn: 307.6 nm</td>
<td>Micro-homogeneity study</td>
<td>(56)</td>
</tr>
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</table>

<sup>a</sup>LOD = limit of detection.
<sup>b</sup>n.a. = not available.
calibration with detection limits of 4.0, 0.16, and 0.02 ng g$^{-1}$ for Fe, Na, and Zn; i.e., elements that are known to be extremely sensitive to contamination. Dokčekal and Krivan (48) reported similar detection limits for the same elements in high-purity molybdenum metal and molybdenum silicide powders. Huang and Krivan (52) determined silicon, another element that is extremely susceptible to contamination, in niobium, titanium, and zirconium oxides with a detection limit around 10 ng g$^{-1}$, again using aqueous standards for calibration. The most decisive contribution to this success obviously came from the fact that no reagents at all were used, or reagents that did not contribute any blank signal. Hornung and Krivan (49, 51) for example used hydrogen as alternate gas in the pyrolysis stage for the analysis of high-purity tungsten, tungsten trioxide and tungsten blue oxide, Huang and Krivan (52) used methane for the analysis of niobium pentoxide, and Krivan and Huang (50) used high-purity carbon powder in the determination of 15 elements in high-purity titanium.

One of the arguments in favor of slurry sampling was that the slurry concentration can easily be changed so that the analyte concentration falls into the analytically useful range of the calibration graph (26). This is true as long as the analyte is 100% extracted into the liquid phase; if this is not the case, slurry sampling is subject to the same limitations as SS ET AAS due to natural inhomogeneity of the small subsamples used, which is not always improved by reducing particle size (53). It has been well established that a minimum number of particles is required for a subsample to be representative for the laboratory sample, independent of the technique used for the analysis (34). Anyway, there are other means available to reduce sensitivity in ET AAS that might be more appropriate than a dilution, such as the use of a gas flow during atomization (54, 55), the use of alternate, less sensitive analytical lines (55, 56), or the use of the three-field Zeeman-effect (56), a technique that has recently become available commercially (57). On the other hand, SS ET AAS is much less affected by the particle size, as sedimentation, etc., obviously do not have to be considered, and even relatively large pieces may be analyzed, such as metal chips (50, 58), pieces of plastic materials (59–61), or wet tissue samples (62, 63). Finally, while the maximum sample mass that can be introduced into the graphite furnace by slurry sampling is around 1 mg (34), an almost two orders of magnitude greater sample mass has been introduced by Krivan et al. (48, 49, 51) for SS ET AAS to improve sensitivity and LOD.

Another topic that has been discussed quite controversially in SS ET AAS is calibration, and it has been stated repeatedly that accurate results could only be obtained using solid standards, i.e., certified reference materials (CRM). Kurfürst (22), for example, writes in his book: “If a CRM is available whose matrix composition and analyte content match that of the sample, ideal analytical conditions are fulfilled”—a situation that can rarely be met in real life. Several authors have compared the three possible basic calibration techniques for SS ET AAS, (a) calibration using solid CRM, (b) the analyte
addition technique, and (c) the standard calibration technique with aqueous standards (64–67), and the errors associated with these calibration techniques. Calibration using one or more solid CRM, besides being expensive and not applicable for routine analysis, was found to contribute significantly to imprecision, as the uncertainty of the certified value is fully introduced into the calibration (66, 67). The analyte addition technique is particularly cumbersome to apply in SS ET AAS, as it is impossible to reproducibly insert the same sample mass into the graphite furnace. The analyte addition technique hence requires a three-dimensional approach, the Generalized Standard Additions Method (GSAM), which takes into consideration the added analyte mass, the response and the sample mass (68). Besides being labor intensive, as a large number of measurements is necessary to arrive at reasonably reliable results, the latter still exhibit rather high uncertainty. However, this problem appears to be kind of academic when Table 1 is consulted, as in essentially all of the manuscripts, with only two exceptions, the standard calibration technique with aqueous standards has been used successfully. This means that interference-free determination could be attained after careful optimization of the analytical conditions. This might include a pretreatment of the sampling platform with the refractory matrix, as in the case of the high-purity materials investigated by Krivan et al. (24, 43, 48–52) and/or the use of a proper modifier (50–52, 61, 69).

Yet another argument that has been brought up in favor of slurry sampling was that chemical modification is easier to perform, because of more effective contact between the sample particles and the modifier (26). However, this effective contact is not necessary for analyte stabilization, as the analyte becomes mobile well before its atomization, and can be efficiently trapped even if it is not been in contact with the modifier (see Maia et al. (70) and the references therein). The fact that analytes can be stabilized by a permanent modifier even when they are introduced as a solid sample was for the first time demonstrated in 2001 for the determination of Cd and Pb in mineral coal, using Ru as permanent modifier (71). This principle has been confirmed later also for the determination of Tl in river and marine sediments (69), for Hg in environmental reference materials (72), and for Cd in coal using Ir as permanent modifier (73). In the case of mercury determination, it could actually be shown that analyte stabilization by a permanent modifier is much more efficient for solid samples than for aqueous standards, which are obviously in much closer contact with the modifier than a solid sample (72).

Last but not least, it has to be mentioned that SS ET AAS is offering a few unique possibilities that are not available with any solution or slurry technique. Firstly, there is the possibility for a very fast screening, essentially without any sample preparation, in cases where only outliers have to be detected that will be investigated more carefully later using other techniques. This possibility has been theoretically evaluated by Belarra et al. (74) using information theory. These authors found that the median can be used to
better effect than the mean value as the former is less affected by the presence of outliers. The minimum number of measurements that need to be carried out to guarantee a recall of over 0.95 in a screening method ranges from 5 to 20, involving between 15 min and 1 h of work. Lücker and Schuierer (62) investigated the sources of error in direct SS ET AAS analysis of fresh animal tissue for screening purposes and found that manual working time and the necessity of operator presence were reduced by at least 80% compared to conventional digestion procedures. Belarra and co-workers investigated the determination of antimony in polyvinylchloride (59), of phosphorus in polyethyleneterephthalate (PET) and polypropylene (61), and of silicon in polyamide (75) also for screening purposes, and claimed a high sample throughput, a precision better than 10%, and low detection limits as the main advantages.

Secondly, SS ET AAS can be used to determine the homogeneity and micro-homogeneity of CRM and other materials (53, 56) and to detect potential outliers (74). Nomura et al. (56) found for a bovine liver sample that both the drying and the grinding process had an influence on micro-homogeneity, which in addition was different for different elements. Belarra et al. (53) also found that lack of homogeneity of the small subsamples used in SS ET AAS is the major source of high RSD values, which is not always improved by reducing particle size. Thirdly, there is the possibility of determining trace element distributions in extremely little samples, such as hair segments, tissue biopsy samples or plant segments, as has been shown by Štupar and Dolinšek (63).

**HIGH-RESOLUTION CONTINUUM SOURCE ET AAS**

The state of the art of high-resolution continuum source AAS (HR-CS AAS) is fully described in a recent book of Welz et al. (76). Although this technique is currently commercially available only with flame atomization, it appears to be more than appropriate to discuss its potential for SS ET AAS in this context, as there are already a number of results available that have been obtained with prototype equipment. The general layout of this system, which is based on preliminary work of Heitmann et al. (77) is shown schematically in Figure 2. It consists of a specially developed xenon short arc lamp, operating in a hot-spot mode for maximum emission intensity in the far UV range, a high-resolution double monochromator with a spectral bandwidth per pixel of 1.6 pm at 200 nm, and a charge-coupled-device (CCD) array detector with full vertical binning. As only an intermediate, but no exit slit is used, a segment of about 0.4 nm of the highly resolved spectrum is reaching the detector and registered simultaneously by 200 pixels of the detector, all of which act as independent detectors.

One of the features of this new concept is that the spectral environment of the analytical line becomes visible at high resolution, as is shown in Figure 3 for the example of Tl in marine sediment CRM. While continuous background
absorption is eliminated automatically, as any of the 200 pixels can be used for correcting spectrally continuous events, spectrally discontinuous absorption, such as atomic absorption of concomitants and molecular absorption with rotational fine structure, become visible. Obviously, any atomic or molecular absorption that is not within the very small spectral window used to measure analyte absorption does not cause any spectral interference. ET AAS in addition offers the possibility to separate analyte and molecular absorption in time by optimizing the temperature program.

Using all these possibilities, Welz et al. (78) succeeded in determining Tl in marine sediment samples without any modifier and calibration against aqueous standards, just by optimizing the temperature program, as shown in Table 2. Using conventional LS AAS with deuterium background correction and calibration against solid CRM it was not possible to arrive at consistent results, even with very sophisticated modifier combinations (69). When the same determination was carried out using LS AAS with Zeeman-effect background correction, an extremely careful selection of chemical modifiers was still necessary, and only a combination of Ru as permanent modifier and the addition of a solution of ammonium nitrate on top of the solid sample resulted in accurate values (69). This actually appeared like a clear indication that the problem originally encountered with deuterium background correction was a combination of spectral interference (which could be eliminated Zeeman-effect background correction) and non-spectral interference (which could only be overcome with a carefully selected combination of modifiers). However, the fact that the same determination could finally be carried out without any modifier and calibration against aqueous standards using HR-CS AAS (78) clearly showed that the interference still encountered with Zeeman-effect background correction must obviously have been of spectral origin, because otherwise it would have appeared as well with the former system.

Figure 2. Instrumental concept for HR-CS AAS (from Welz et al. (82)).
The concept was later extended to the determination of Tl in mineral coal and the only condition that had to be met was a pyrolysis temperature higher than 600°C in order to avoid excessive continuous background absorption due to radiation scattering at volatilized particles. Using a pyrolysis temperature of 700°C, this problem was solved, and no modifier was required for the determination of Tl in coal (79). Cadmium could be determined in coal under the same conditions, i.e., using a pyrolysis temperature of 700°C, which, however, required a chemical modifier to stabilize Cd, and Ir as permanent modifier was found optimum for that purpose (73). It is interesting to note that the same determination of Cd in coal, using the same equipment, but slurry instead of direct SS ET AAS could not be carried out satisfactorily, as the maximum applicable pyrolysis temperature in this case was only 600°C (80). This appears to be the first case where under otherwise identical analytical conditions, the direct SS ET AAS method succeeded, whereas the slurry method failed. Another application has been the determination of Co in a variety of biological materials, which also did not require any modifier and could be carried out against aqueous standards after program optimization (81).

It has to be mentioned that HR-CS AAS, in addition to the above features, has the advantage that, due to the use of a high-intensity continuum source, all

**Figure 3.** Atomic and molecular absorption signals observed during the atomization of a marine sediment sample in the vicinity of the Tl resonance line at 276.787 nm using SS HR-CS ET AAS (from Welz et al. (78)).
Table 2. Determination of thallium in marine sediment reference materials (CRM) using direct solid sampling ET AAS and three different instrumental concepts: Deuterium background correction with calibration against a solid CRM (from Vale et al. (69)), Zeeman-effect background correction with calibration against aqueous standards (from Welz et al. (78)) and HR-CS AAS with calibration against aqueous standards (from Vale et al. (78)).

<table>
<thead>
<tr>
<th>CRM</th>
<th>Reference value&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ETV-ICP-MS&lt;sup&gt;b&lt;/sup&gt;</th>
<th>D&lt;sub&gt;2&lt;/sub&gt; correction</th>
<th>Zeeman-effect background correction</th>
<th>HR-CS AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ru/ NH₄NO₃&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Without&lt;sup&gt;d&lt;/sup&gt; NH₄NO₃&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Ru/ NH₄NO₃&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>BCSS-1</td>
<td>(0.6)</td>
<td>—</td>
<td>0.36 ± 0.03</td>
<td>—</td>
<td>0.59 ± 0.04</td>
</tr>
<tr>
<td>HISS-1</td>
<td>(0.06)</td>
<td>0.055 ± 0.004</td>
<td>0.04 ± 0.01</td>
<td>0.02 ± 0.002</td>
<td>0.05 ± 0.003</td>
</tr>
<tr>
<td>MESS-1</td>
<td>(0.7)</td>
<td>—</td>
<td>0.42 ± 0.05</td>
<td>—</td>
<td>0.70 ± 0.02</td>
</tr>
<tr>
<td>MESS-2</td>
<td>(0.98)</td>
<td>0.99 ± 0.04</td>
<td>0.87 ± 0.03</td>
<td>0.19 ± 0.01</td>
<td>1.07 ± 0.03</td>
</tr>
<tr>
<td>MESS-3</td>
<td>0.90 ± 0.06</td>
<td>—</td>
<td>0.85 ± 0.10</td>
<td>—</td>
<td>1.08 ± 0.07</td>
</tr>
<tr>
<td>PACS-2</td>
<td>(0.6)</td>
<td>0.52 ± 0.02</td>
<td>0.21 ± 0.06</td>
<td>0.12 ± 0.03</td>
<td>0.58 ± 0.02</td>
</tr>
<tr>
<td>SRM 1646a</td>
<td>(&lt;0.5)</td>
<td>—</td>
<td>0.10 ± 0.02</td>
<td>—</td>
<td>0.20 ± 0.02</td>
</tr>
</tbody>
</table>

<sup>a</sup>Values in brackets are not certified.

<sup>b</sup>Values taken from Maia et al. (41).

<sup>c</sup>400 μg Ru as permanent modifier + 20 μL of 5% w/v NH₄NO₃ added to the solid sample.

<sup>d</sup>Without use of a modifier.

<sup>e</sup>Twenty microliters of 5% w/v NH₄NO₃ added to the solid sample.

All values are in μg g⁻¹, and average and standard deviation of n = 3.
analytical lines are available without any compromise regarding the signal-to-noise ratio; i.e., there are no more “weak lines.” Another possibility offered by this technique is that in addition to the usual evaluation of the line center using 1–3 pixels, there is the possibility to evaluate the absorbance at the line wings only in order to reduce the sensitivity and expand the linear dynamic range to some five orders of magnitude. This appears to be particularly important for SS ET AAS to reduce the sensitivity in cases where no secondary line of appropriate sensitivity is available, such as in the case of Cd or Zn. It is of particular importance that this extension of the working range does not require a new measurement, as a whole set of calibration curves can be established simultaneously. All these possibilities obviously have yet to be explored, but the expectations for this excitingly new technique are high for good reasons.

CONCLUSION

Direct SS ET AAS has matured significantly during the past decade, and with proper accessories for sample introduction being available it can be considered a rugged technique ready for routine application. A relative standard deviation (RSD) of the order of 10%, as it is typical for this technique due to the naturally inhomogeneous distribution of trace elements in the relatively small subsamples, should not be considered a major limitation. In the opinion of the present authors a 10% RSD of an accurate result is much more acceptable than a 1% RSD of a result that is affected by systematic errors due to analyte loss or contamination during sample preparation. Direct SS ET AAS is not affected by problems such as sedimentation or partial leaching of the analyte, and particle size is much less critical than in slurry sampling. It is fast, offers the lowest LOD, and has a significant contribution to clean chemistry. HR-CS AAS is expected to further enhance the attractiveness of SS ET AAS, making it even simpler to use and more flexible in its application.

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