Digestion or Direct Solid Analysis – A Fast and Precise Technique for Trace and Ultra-trace Analytics

The main problem in modern trace analysis is to ensure correctness of data. Methods, which only require a small number of sample preparation steps, are extremely advantageous, as they minimise the risk of contamination. Besides time savings, one of the major advantages of determining trace elements directly as solids is the avoidance of contamination of the sample from the solvent during sample digestion. Analytik Jena makes this possible with the automatic solid sampler SSA 600 (Figure 1).

The classical methods of sample preparation for atomic spectroscopy include various digestion techniques. The associated investment in time and personnel limits the sample throughput achievable in the analytical laboratory. Reagents are required, both for digestion and for the subsequent steps, such as dilution, which, along with the vessels and handling of the samples, can lead to contamination and inaccuracy.

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The classical digestion techniques offer the advantage that the sample matrix, especially of organic samples, is largely removed, leaving a clear, homogenous solution, which can be analysed with any chosen method. However, correct analysis results necessitate a sufficient quantity of the homogenous sample and highly pure reagents. Thorough cleaning of the vessels used and conscientious handling of the sample are essential.

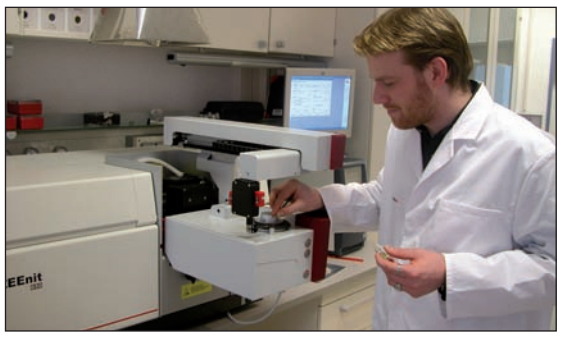


Figure 1. Fully automated SSA 600 solid sampler with integrated microbalance.

To circumvent many of these sources of error, analysis techniques have existed for some time now with which solids can be directly analysed. Among the best known are X-ray fluorescence analysis (XRF) and laser ablation ICP-MS. Both techniques still require a considerable amount of apparatus and financial resources, as well as expert knowledge and experience in the respective areas; especially calibration can sometimes be extremely tricky.

Graphite tube AAS combined with a solid autosampler unifies the advantages of solid technology with the simple operability of AAS. It reduces both the use of reagents and sampling handling to a minimum; it is also suitable for the smallest sample quantities.

Depending on the nature of the sample, it may be necessary to homogenise it with the aid of a grinder and to produce a suitable particle size. A small quantity of sample (approximately 50 - 5000 µg) is then dosed onto a graphite platform and, following fully automated weighing on the integrated microbalance, is decomposed with the relevant modifier – finished! The solid autosampler takes care of transporting the platform between the sample tray, balance and graphite tube.

The measurement itself takes place with a temperature-time programme (TTP), as is standard practice in the graphite tube, also for liquid samples. For solids, the TTP may appear more complex than is usually the case, as pyrolysis replaces the other sample preparation steps. Depending on the sample composition, there may be many other matrix components present during the measurement, which necessitate effective background correction.

Various options are available for calibration. Reference materials are preferred whose composition largely matches that of the sample. Ideally, various materials in different analyte concentrations are available for use, but also different weights of the same material can be used. If such materials are not available, in many cases one can resort to calibration with liquid standards; a standard addition with solid or liquid standards is also possible.

MEASUREMENT AND RESULTS

Two examples are presented, which put the potential of the system to the test. The first part of the investigation involves the determination of heavy metals in wood. In the second part, the results of measurement of various plant samples are compared. The investigations were performed in parallel with the solid autosampler from Analytik Jena and with the conventional graphite tube AAS following microwave digestion.

Part 1

The city of Huelva in South West Spain is a well-known industrial city. The investigations are centred on the industrial park near the city on the Rio Tinto River. Here there is a waste landfill site where deciduous trees grow. The landfill body contains waste from a copper smelting plant in southern Spain. The waste contains many heavy metals and heavy metal compounds from the copper smelting plant. The pH value in the landfill body is between 3.2 and 5. The temperatures are around 40 degrees Celsius in the summer and there is some torrential rainfall.

The analysis of the trees on the landfill site serves to investigate the mobility and the bioavailability or various selected heavy metals. The investigations are also intended to represent a time profile. As deciduous trees form identifiable annual rings in their wood, these can be used to trace the pollutant uptake in the respective year.

Sampling

Samples were taken from the trunks of trees growing directly on the landfill site, as well as from trees close to the landfill site. The samples were dried and cut into thin slices. The annual rings were separated out of these slices and any surface contamination removed. Small pieces were then cut out of the annual rings and 250 – 750 µg (depending on the element content) was weighed in each case.

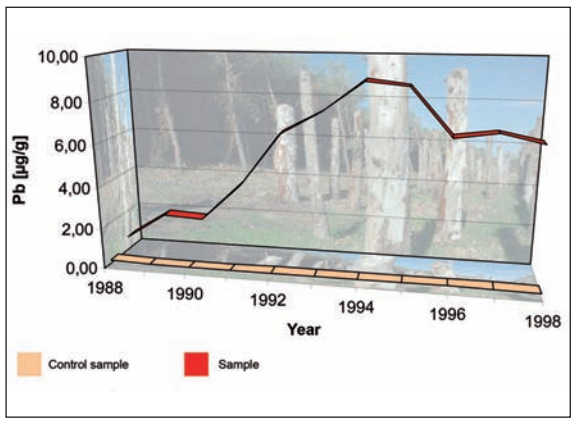


Figure 2. Concentration of lead in wood over a period of 10 years.

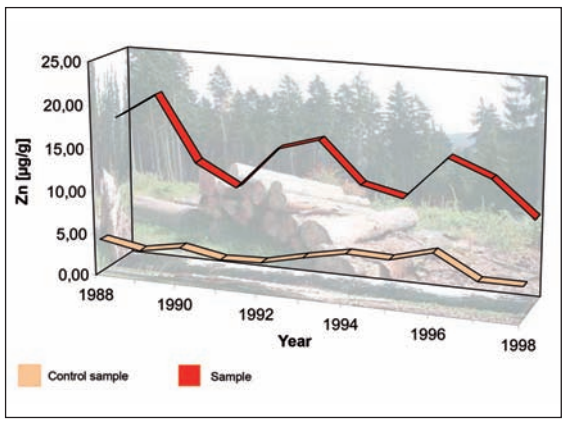


Figure 3. Concentration of zinc in wood over a period of 10 years.

The investigations were carried out for the elements lead, zinc, copper, manganese and nickel. The results show that heavy metals are mobilised and taken up by the trees under the given conditions. From the example of lead (*Figure 2*), it may be seen that the concentration of the element in wood rose sharply from the end of the 1980s to the mid 1990s. From the mid 1990's the concentration of lead declines and stagnates thereafter. The concentration of the element zinc (*Figure 3*) in wood shows a fluctuating profile in the period from the end of the 1980s through to the

1990s with a slight downward trend. When interpreting the results, varying climatic and geological conditions, for example, long periods of drought, groundwater flow speed and sorption of heavy metals from the soil, must of course be taken into consideration.

Part 2

To ensure that the solid technique achieves correct results, selected plant samples were analysed directly as solids and also in the form of a digestion solution.

The solid analysis involved firstly grinding and homogenising the samples for 3 minutes in a ball mill (MM2000, Retsch GmbH, Haan, Germany). Weights of around 200 – 400 µg were then directly analysed by graphite tube AAS.

For comparison, approx. 0.5 g of each sample was subjected to microwave digestion (Multiwave 3000, Anton Paar GmbH, Graz, Austria). The clear solution obtained was filled to 50 ml and also analysed by means of graphite tube AAS.

The element content measured with Zeeman background correction using both techniques are compared in *Table 1*.

Table 1. Comparison of measurement values between direct analysis of solid and solution.

Sample	Cd solid [µg/kg]	Cd digestion [µg/kg]	Pb solid [µg/kg]	Pb digestion [µg/kg]
Herbs 1	22.0	23.2	131	135
Herbs 2	64.3	70.2	866	856
Green tee	24.2	25.9	236	231

DISCUSSION

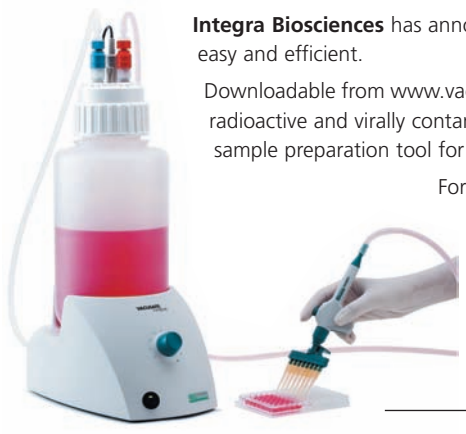
Investigation using the solid technique offers the user significant advantages. The time-consuming digestion technique is avoided, the measurements can be performed faster, and sources of error are excluded. The wood sample measurements in Part 1 effectively illustrate the effectiveness of the method. Comparison of the measurement results from solid autosamplers and from the conventional sample digestion technique in Part 2 shows good correlation and confirms the comparability of the two techniques for investigations of this type.

There are, however, some limitations in the application of the solid sample technique. The use of this technique can, for example, be critical for elements with very high atomisation temperature, such as molybdenum and titanium. As with the classical digestion methods, the analysis of inhomogeneous samples can lead to erroneous results. On the other hand, this can be advantageous in studies of sample homogeneity.

A limitation for inhomogeneous samples of this type therefore lies in the low repeatability compared with conventional sample digestion. As the complete sample is digested as a whole and a homogenous solution is produced, the deviation is naturally not so large.

However, the advantages that solid sample technique has to offer are decisive: analysis of the original sample without the addition of reagents; fast analytic method, as no sample preparation is required; true micro-method, as only small sample quantities (50 µg - 5 mg) are required; reduced analytical error, e.g. contamination, blank value and dilution errors; high sensitivity and very good detection limits – therefore suitable for trace and ultra-trace analysis; economical, as no additional chemicals and laboratory equipment are required; ecological, as environmentally polluting chemicals are avoided; and very well suited for homogeneity studies.

Applications Reports Demonstrate Safe and Efficient Aspiration of Liquids



Integra Biosciences has announced 2 new applications reports that demonstrate how it's personal vacuum aspiration system - VACUSAFE comfort makes the aspiration of liquids safe, easy and efficient.

Downloadable from www.vacusafe.info – the first application report shows how the VACUSAFE comfort is enabling a leading North American hospital to safely and productively aspirate radioactive and virally contaminated solutions. A second downloadable application report discusses how a European company is using the VACUSAFE comfort as a safe and productive sample preparation tool for their high-throughput molecular diagnostic kits.

For laboratories tired of inflexible and noisy vacuum systems – VACUSAFE comfort makes aspiration of hazardous liquids very safe, user-friendly and flexible. The compact, all-in-one vacuum aspiration system incorporates low-noise pump, shatterproof collection bottle and a versatile hand operator. With its adapters, removal of liquids is possible from virtually any container. It is extremely simple to operate - switch on, set the required vacuum and start working. Unlike most 'home-made' aspiration systems, the VACUSAFE comfort has several important safety features like the liquid level sensor and the two hydrophobic filters that block potentially dangerous aerosols. VACUSAFE comfort is the laboratory vacuum of choice for a growing range of life science applications where gentle and controlled removal of supernatants is required.

Circle no. 71

Fume Hoods Certification

Esco is pleased to announce that the Frontier Acela Fume Hood (EFA), 4', 5' and 6' widths, have been certified by Tintschl Engineering AG, Germany to the stringent European Standard EN14175-3.

Frontier Acela combines key aspects of the patented Berkeley Fume Hood technology with unique Esco innovations, to deliver the industry's premium fume hood solution. EN certification further affirms Esco's commitment to providing customers with hoods that can achieve maximum containment at low face velocities, thus saving energy without compromising safety.

Selecting the Frontier Acela Fume Hood will reap benefits for all stakeholders involved. Health and safety authorities will benefit from: ASHRAE 110 and EN14175 tested at face velocities down to 0.3m/s (60fpm); built in sash-lock and creep-down system ensure operator safety; and optional Sentinel XL Airflow Monitor. Facility owners can operate at 0.3m/s (60fpm) at 457mm (18") operating height and will see energy savings of up to US$5,735 annually for each fume hood. Laboratory designers and architects will benefit from a neutral colour scheme; futuristic design; and detailed architectural specifications and drawings. Installation and service personnel will see advantages in robust tri-wall side pan construction; factory-fitted service fixtures are pre-plumbed; chain and sprocket sash; and a wide range of field-installed accessories. Laboratory personnel will benefit from certified safety; precisely tuned aerodynamics; high sight line; angled front; and excellent ergonomics.

Circle no. 72

New Options for Twin Filter Face Masks

The lightweight **Draeger** X-plore 3000 Series of twin filter half-masks is ideal for use in any environment where airborne dusts and metal particles might be found. Combining comfort and FFP3 levels of performance, the range also offers a wide choice of design options to suit different users as well as different environments. The Draeger X-plore 3300 limited life version is ideal for those requiring an economical yet comfortable respirator for short duration, one-off applications, whilst the X-plore 3500 offers robust, reusable protection for longer-term wear. Available in three sizes and easily adjusted to ensure an optimum fit for different face shapes, the range also features an innovative X-guided strap system to ensure an even weight distribution. In addition, the 3500 incorporates a revolutionary 'drop down' design to allow easy removal without, for example, having to remove a safety helmet.

Specifically designed to suit any head shape, a new FlexiFit head cradle eliminates hair entanglement as well as pressure points, and is almost unnoticeable beneath a safety helmet. The low profile, 'swept back' design ensures an optimal field of vision when worn with protective visors, and a flexible nose section affords a secure seal whilst offering excellent compatibility with safety glasses and goggles. Simple to don and straightforward in use, each of these masks also feature an easy, secure bayonet filter attachment. As a result, they can be used with a wide selection of filters including the new Draeger X-plore Pure Filter range. Reusable over more than one shift and featuring a patented design for a quick and easy fit, the Pure, lint-free filters can be used as a particle filter or in combination with gas filters. Modular in design, they can also be supplied with an integrated charcoal layer to protect against nuisance and organic odours.

Circle no. 73