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Analytical Minimalism Applied to the Determination of Trace Elements by Atomic Spectrometry*

Invited Lecture

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In analytical minimalism, each stage of the analysis is evaluated to minimize the time, cost, sample requirement, reagent consumption, energy requirements and production of waste products. These parameters are often inter-related. If the objective of digestion of biological tissues, foodstuffs and environmental samples is taken as the complete dissolution of the trace elements, then the time of digestion by conventional heating can be reduced considerably to times comparable with pressure digestion using microwave heating. The development of rapid and simple partial digestion techniques is reviewed. In electrothermal atomic absorption spectrometry, by assessing the function and time of each stage in the programme, it has been possible to reduce the programme time to about 30 s for a number of determinations. Recent developments in fast furnace technology are reviewed, particularly on omission of the ashing stage and drying with hot injection or high temperatures. With reduction in furnace programme time, the time taken by the autosampler (30–35 s) becomes dominant. Developments to reduce this time by 10–20 s are discussed. In the evaluation of results, minimal time and effort by the analyst is ensured by customized computer programmes. The programmes, variants of one or two basic programmes, are adapted for each determination to retain the value of standards, to correct for blanks and to allow conversion from g l^{-1} to mol l^{-1}.

Keywords: *Partial digestion; electrothermal atomic absorption spectrometry; fast furnace analysis; clinical and biological samples; analytical minimalism*

The aim of analytical minimalism is to keep analytical processes as simple as possible with the minimum consumption of resources. Parameters that should be minimized are time, cost, sample requirements, reagent consumption and waste production. Reduction in time is of particular relevance as this increases throughput and reduces costs. As will be apparent, many of these parameters are inter-related. For example, a reduction in sample volume generally leads to a reduction in reagent consumption and production of waste products. All processes carried out in the laboratory, from sample handling to calculation of results and report generation, need to be considered in this way. The purpose of this paper is to demonstrate some aspects applied to the determination of trace elements by atomic spectrometry particularly in clinical and biological samples and to review progress in fast furnace analysis in electrothermal atomic absorption spectrometry (ETAAS).

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SAMPLE PREPARATION

Sample Amount

In the clinical field, it is becoming more and more relevant to work with small amounts of sample. Commercial multichannel analysers for general clinical chemistry produce a wide range of results from a small volume of sample so that clinicians expect more specialized tests to be produced from a small quantity of blood. This is imperative for samples from neonates and infants from whom the total blood volume sampled must be limited. Athough determination of copper in blood plasma from adults is more economically and rapidly carried out by flame atomic absorption spectrometry (FAAS), for samples from neonates and infants, ETAAS is more appropriate, as the sample volume can be limited to 20 μl.[1,2] The determination is particularly relevant for premature infants, who have limited copper stores, because most of the copper stores in the infant are laid down in the third trimester of pregnancy.[3] Failure of the neonate to absorb sufficient copper in its early life can lead to brittle bone formation as a result of a failure to produce sufficient collagen and elastin cross-linking.[4]

Measurement of iron and copper in the liver is invaluable in confirmatory diagnosis of haemochromatosis and Wilson's disease, respectively. Biopsy samples taken by needle may weigh as little as 2–4 mg after drying. Care is needed in handling the specimen (particularly to avoid losing it!). Once dissolved in acid, determination is straightforward by FAAS for iron or ETAAS for copper (Fig.1).

Small scale working was necessary in the development of a method for the determination of arsenic in hair by ETAAS.[5]

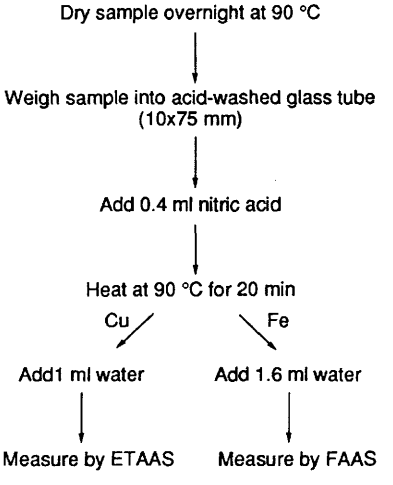

Fig. 1 Procedure for the determination of Cu or Fe in liver biopsies. For each determination, blanks and a reference material, BCR No. 165 Bovine Liver, are put through the same procedure

As this was intended to replace a previous method using neutron activation analysis, the sample requirement of 3–10 mg of hair preferably had to be retained. To obtain adequate sensitivity, the sample was dissolved in 100 µl nitric acid, taken to dryness and re-dissolved in 100 µl of 1% v/v nitric acid. This was mixed with 100 µl of palladium modifier (1 mg l^{-1}) for analysis.

Digestion of Samples

In recent years, advances have been made in reduction of the time of preparation of solid samples by slurry sampling[6,7] and bomb digestion with microwave heating.[8] Applications to the analysis of clinical and biological samples have been reviewed in recent Atomic Spectrometry Updates.[9–12] In most publications, comparison is generally made with classical wet digestion techniques, which take several hours to complete. Most of the wet digestion techniques date back to the days of colorimetric analysis, when it was essential to remove all traces of organic material.[13] Even recently these objectives have been seen as important and have been studied for a range of digestion procedures.[14,15] For most atomic spectrometric analysis, a more relevant objective is the complete dissolution of the trace elements to be measured. Many practical analysts have realized that it is possible to achieve this with simpler procedures. Extraction with dilute acid at room temperature is effective at releasing Ca, Cd, K, Mg, Mn, Na, Pb and Zn from biological tissue,[16,17] but not Cu[17,18] or Fe.[16–18] Luterotti *et al.*[19] determined Cu, Mn and Zn in rat liver by homogenizing the material with five times the mass of water, adjusting the HCl concentration to 1 mol l^{-1}, shaking for 30 min and centrifuging the resulting mixture. The elements were determined in the supernatant by FAAS. Treatment at a higher temperature speeds up extraction.[20] Price[21] quotes a procedure by Premi and Cornfield[22] in which Cu, Cr, Fe, Mn and Zn were quantitatively extracted from plant materials and sewage sludge by boiling with 6 mol l^{-1} HCl. Using citrus leaves as a model for plant material, Bassen and Böhmer[20] found that Ca, Cu, K, Mg, Mn and Zn were completely extracted after heating with 3 mol l^{-1} HCl for 15 min but Fe was not. Kuennen *et al.*[23] found that moderate pressure produced by digesting samples with 6 mol l^{-1} HCl in capped polyethylene bottles at 80 °C for 30 min was effective in extracting a range of elements from agricultural crops, including Fe. After an evaluation of various hot-plate procedures and room temperature digestion for bovine liver, Asp and Lund[18] recommended a simple procedure based on heating with HNO_3 for 1–2 h, followed by filtration of undissolved material. Accurate results were obtained for Cd, Cu, Fe, Mn, Mo and Zn in certified reference materials on determination by inductively coupled plasma atomic emission spectrometry (ICP-AES).

In a recent study,[24] minimization of the time required for complete extraction of the elements Cu, Fe, Mn and Zn from biological tissues was addressed. For Community Bureau of Reference (BCR) Bovine Liver and Pig Kidney reference materials (RMs) and for fresh bovine liver, these elements were completely extracted after heating with HNO_3 at 105 °C for only 20 min. Digests were centrifuged after dilution and the elements determined by FAAS, ETAAS or ICP-AES. Good agreement was shown with results by complete digestion and results on RMs were in good agreement with certified values. This approach has also been used successfully in the determination of the same four elements in a range of foodstuffs.[25] A similar approach was used by Zima *et al.*[26] for the determination of Cd and Pb in animal tissues. After boiling the samples with HNO_3 for 15 min, the digests were made up to volume with ethanol to prevent undigested lipids from precipitating.

In Table 1, a comparison is made on the basis of the minimization parameters discussed earlier, between the partial digestion technique and a rapid microwave bomb digestion procedure described by Van Wyck *et al.*[27] for the determination of iron in tissue. Although the heating time is five minutes longer by partial digestion, the cooling time is considerably shorter and the overall time is shorter. Undoubtedly, the time by microwave digestion could be shortened, but the important point is that the times are comparable. Microwave heating is more efficient in energy consumption than a block heater because pre-heating is unnecessary. In cost of reagents and production of waste products, there is very little difference. However, the capital cost of a laboratory microwave digestion system with bombs far exceeds the cost of a block heater. If the bomb digestion is carried out in a domestic microwave oven, the capital cost of equipment is less than a block heater. Whether this is desirable because of safety considerations is a contentious issue,[28,29] which will not be pursued here. The important conclusion is that the partial digestion approach offers an alternative to the cost and complexity of a laboratory microwave digestion system. Another obvious inference is that a combination of the partial digestion approach with microwave heating would be more energy efficient. An indication of the potential of this is seen in the work of Blust *et al.*,[30] in which brine shrimp samples were digested directly in polypropylene autosampler cups with 100 µl HNO_3 for 5 min with microwave heating. Water (1 ml) was added and the samples analysed by ETAAS.

This approach of partial digestion has been applied to the routine determination of Cu and Fe in liver biopsies (Fig. 1) in order to reduce digestion time. It has been found possible to omit the centrifugation step used in the preliminary work,[24] further simplifying the procedure.

DETERMINATION BY ETAAS

One of the drawbacks of conventional determination by ETAAS is the prolonged time required to produce a result. In 1983, Bahreyni-Toosi and Dawson[31] produced a miniature graphite furnace with Zeeman-effect background correction to allow determinations in a single step. Although the objective of a single step has not been achieved since, the work did show

Table 1 Comparison of microwave bomb digestion and partial digestion for preparation of tissue samples for determination of iron

	Microwave bomb digestion[27]	Partial digestion[24]
Procedure	250 mg sample + 1 ml HNO_3 + 1 ml H_2O_2	100–200 mg sample + 2 ml HNO_3
Time	15 min at 25% power 30 min cooling	20 min at 105 °C 10 min cooling 5 min centrifugation
	Total 45 min	Total 35 min
Energy consumption	0.150 kW h^{-1}	0.167 kW h^{-1} +0.250 kW h^{-1} for preheating
Waste products	Fumes on opening bomb	Fumes during digestion
Approximate capital cost (1994 prices)	£10 000	£650
Reagent cost and consumption	Very low	Very low

the potential time saving of this technique. Practical steps to reduce programme time with conventional furnaces then followed.[32] The purpose of this section is to review progress that has been made over 10 years. Developments are discussed under the four main steps in a furnace programme, drying, ashing, atomization and clean. A further section covers the time taken by the autosampler.

Drying Stage

In conventional programmes, the time allocated to drying can be quite extensive. Three approaches have been tried to reduce the time in the drying stage; minimization of the time in conventional drying, injection of the sample onto a preheated tube ('hot injection') and high-temperature drying.

Conventional drying

Most graphite furnace systems display temperature and allow ramped temperature programming. The temperature displayed is, in most cases, a function of the power applied to the tube and is not a reading of actual temperature. Because of the thermal mass of the graphite, the actual temperature will lag behind the programmed temperature when ramping. Studies[32] of the actual temperature attained in a drop of water on the surface of an uncoated graphite tube showed that ramp times of 1–7 s made no difference to the shape of the temperature rise seen. Distinct temperature ramps were seen at programmed ramp times of 10 and 20 s. As the natural temperature response provided ramping of around 100–140 °C, the applied temperature ramp was set to the minimum time (1 s) and drying times of 7–12 s were used. Pyrolytic graphite coated graphite surfaces are more hydrophobic and more care is needed in drying. Table 2 shows minimized drying stages suitable for simple matrices for the three types of graphite surface commonly used. Since temperature settings vary between instruments, some experimentation with the applied temperature setting may be necessary to obtain satisfactory drying. Although atomization from pyrolytic graphite coated tubes or from platforms may offer higher sensitivity and possibly lower interferences, for many applications uncoated graphite tubes provide adequate sensitivity and freedom from interferences and have the advantage of simpler and more rapid drying stages, particularly with serum and urine.[2,32]

Hot injection

The ability to dry samples almost instantaneously by injecting samples onto a pre-heated tube is now available on a range of graphite furnace systems. Control of the pipetting speed is important as the rate of sample introduction needs to be slowed down so that the sample is almost immediately dried as it contacts the tube surface, which is kept at temperatures of 100–120 °C. If the ashing stage is omitted, the injection needs to be followed by a purge stage to ensure that water vapour is completely removed before atomization. Knowles[34] applied hot injection to the determination of Cr, Cu and Ni in water, Cd and Cr in urine and Cu in serum, thus reducing programme times to <20 s. Procedures for the determination of Al, Cu and Pb in waters and Cu, Fe, Ni and Pb in biological RMs were developed by Kunwar *et al.*[35,36] The technique is ideally suited for the analysis of chelates extracted into isobutyl methyl ketone (IBMK), as Apostoli *et al.*[37] demonstrated for the determination of V in urine by extraction with cupferron. Comparison with conventional drying showed an improvement in precision and a three-fold improvement in sensitivity, which was presumed to be due to reduced formation of vanadium carbide. The versatility of the hot injection approach has been shown in a series of application notes from Varian, which include the determination of Ag, As, Bi, Cd, Pb, Sb and Se in stainless steel;[38] As, Cu and Pb in seawater;[39] Cd in blood;[40] Cd and Ni in shellfish tissue;[41] Cu in urine;[42] Pb, Tl, Bi, Cd and Sn in high purity sulfuric acid[43] and Se in blood and urine.[44]

A further approach, which has an even longer history, is to spray an aerosol of the sample onto a pre-heated tube. The system, originally developed by Matousek[45] and marketed by Thermo Jarrell Ash as the Fastac system, is based on a pneumatic nebulizer of the type used in FAAS. A disadvantage is that not all the sample reaches the atomizer, as in FAAS, and hence sample volume requirements are greater with this technique. This is overcome by thermospray introduction, as Bank *et al.*[46,47] have shown. In their system, a fixed volume (normally 10 µl) of sample was introduced into a flow injection system which pumped the sample through a heated fused silica capillary and deposited the thermospray onto a pre-heated graphite tube or platform. To avoid condensation of water vapour on the windows of the furnace, an evacuation system was necessary to remove the water vapour generated.

High temperature drying

A third approach is to apply indicated temperatures much higher than would normally be thought acceptable for drying. If conditions are chosen correctly, drying occurs without sputtering and results with good precision are obtained. For wall atomization on uncoated tubes, it was found possible to apply drying temperatures of up to 260 °C without loss of precision. Methods for the determination of aluminium and lead in waters were developed without an ashing stage using a drying temperature of 250 °C.[48] The use of high drying temperatures also helped to expel water vapour rapidly from the tube, which was shown to be important to eliminate interference in the determination.

For platform atomization, Slavin *et al.*[49] heated the platform rapidly by applying an indicated temperature of 700 °C for 1 s and then dried at 400 °C. The total drying time was 18 s. The minimum time and temperature for drying of slurries on pyrolytic graphite platforms was studied systematically by Hinds *et al.*[50] For drying temperatures in the range 200–500 °C, the minimum time required for drying was established for volumes of 10 and 20 µl of slurry. The time decreased with an increase in temperature and a decrease in sample volume. Temperatures above 400 °C resulted in shoulders and double peaks (probably owing to sputtering). The drying stage chosen for 20 µl aliquots was an applied temperature of 400 °C with a ramp time of 1 s and a hold time of 20 s. These findings were confirmed by Lopez Garcia *et al.*[51] for the analysis of slurries of diatomaceous earths. They reduced the drying hold time to 15 s.

In all of these cases, it seems unlikely that the temperature actually reaches the applied temperature setting. The greater

Table 2 Drying stages for simple matrices

Graphite tube	Temperature/°C	Ramp time/s	Hold time/s	Example	Ref.
Uncoated	140	1	7	Cu in urine	32
Pyrolytic graphite coated	130	1	15	Cr in plant digests	33
Platform with pyrolytic graphite coated	160	1	15	Pb in plant digests	33

power applied to the furnace causes a more rapid rise in temperature which allows drying of the sample in a very short time, probably when the surface of the tube or platform reaches $\approx 100\,^{\circ}C$.

Ashing or Pyrolysis (Charring) Stage

In a conventional heating programme, this stage can take a substantial proportion of the total programme time. The functions of an ashing stage are summarized in Table 3. If the ashing stage achieves none of these functions then it is unnecessary and can be omitted. For samples with high organic content, omission of the ashing stage causes generation of smoke in the atomization stage which obscures and scatters the incident light, giving rise to high background absorbance. Biological, food or environmental samples, which have been digested, or blood samples, which have been deproteinized, have had their organic content largely removed which makes it possible to consider omission of the ashing stage. The ability of an ashing stage to remove compounds that give rise to background absorbance or chemical interferences is often very limited. Except for measurements at very low wavelength (*e.g.*, for As and Se), background absorbance for most biological samples is from sodium and potassium chlorides which cannot be removed until temperatures of $\geqslant 1000\,^{\circ}C$ are achieved. For determinations such as Cu in urine,[32] for which the maximum ashing temperature is 900 °C, ashing makes no difference to the background absorbance or the matrix effect and can be omitted. For others (*e.g.*, Cr in urine[52]), the background absorbance without an ashing stage is still within the range correctable with a D_2-arc system. The use of Zeeman-effect background absorbance offers even greater possibilities for omission of the ashing stage.[49] With respect to the last function of the ashing stage (Table 3), matrix modifiers should be avoided unless really necessary. Slavin *et al.* have shown that it is possible to get accurate analyses without a modifier and without an ashing stage for a range of digested[49] and slurried samples.[53] Under these conditions, the peak shapes for the same element vary more greatly from matrix to matrix than with conventional programmes with modifiers, as Hoenig and Cilissen observed.[54] They concluded that the use of integrated absorbance measurement for volatile elements was necessary under these conditions. Table 4 lists published fast furnace methods showing many examples where the ashing stage could be omitted.

When the ashing stage cannot be omitted, then the ramp and hold time should be minimized. After 30 s, very little further change in background absorbance occurs and times in excess of this are rarely necessary. It is only necessary to reduce the background absorbance to a level that the correction system can cope with. For many samples, the main function is to remove organic material and the time can be kept short (*e.g.*, Cu in serum[2]).

In many graphite furnace systems, the gas flow is automatically reduced at a fixed time interval before atomization begins in order to stabilize gas flow. As this normally means zero or very low gas flow, products vaporized in this time will not be swept out of the tube before the atomization stage begins and could interfere in the atomization. This needs to be borne in mind when minimizing the ashing time. When the ashing stage is omitted, this affects the drying stage. Thus with Perkin-Elmer graphite furnaces (except the HGA 500) programmed for zero gas flow in atomization, gas flow is switched off 5 s before the start of the atomization stage and so 5 s needs to be added to the drying stage in Table 2 when the ashing stage is omitted.[32]

Table 3 Functions of a charring or ashing stage

1. To remove organic material.
2. To remove compounds which give rise to background absorption.
3. To remove compounds giving rise to matrix effects.
4. To facilitate reaction with a modifier.

Atomization Stage

This measurement step is normally one of the shortest stages in the furnace programme. The time required is evident from the video display of the peak shape and so there is little that needs to be changed from current practice.

Clean Stage

In procedures developed in this laboratory, the clean step has been retained but reduced to a time of 3 s at 2700 °C,[2,32,48] except when there was evidence of carryover, in which case the time was increased to 5 s.[52] Lopez Garcia *et al.*[51] omitted the clean step from their programmes for the analysis of slurries of diatomaceous earths. On testing omission of this stage for the determination of lead, they found no loss of sensitivity or precision but a slight increase in background signal over the first 6–7 injections finally reaching a plateau. On the basis of their experience, it would seem worthwhile examining, for all determinations, whether this stage is necessary. Certainly for atomization at high temperatures (2500–2700 °C), a further step at a similar temperature may not achieve much more in matrix removal. For refractory elements, however, it seems unlikely that the clean step could be omitted without introducing carryover.

Sampling Time

As it became possible to shorten furnace programmes, it became obvious that the time taken by the autosampler also needed to be reduced if further reduction in time was to be made. Times taken by some commercial autosamplers are shown in Table 5; separate addition of modifier increases these times. Varian recommended that a volume of blank should be taken up before the sample, allowing the blank to wash out the sample.[65] Depending on the relative positions of the sample and blank, times of between 38 and 42 s were measured. For most samples this is unnecessary and the time then reduces to 33 s. In all these examples, the processes of rinsing the tip and injection start only when the furnace programme is complete. Measurement of the temperature decrease of the surface of a L'vov platform in a tube after heating at 2500 °C showed[33] that the tube had cooled down to under 100 °C after about 20 s, allowing a potential reduction in time of about 10 s. A device was built for Perkin-Elmer AS1 and AS40 samplers, which allowed them to be controlled by the furnace programmer so that the sampler could be started before the furnace programme had ended. Details of this have been published,[66] showing that time savings of 15 s are possible with an uncoated tube, and that using a more conservative 10 s saving gave satisfactory results in routine use. Further trials of routine operation with a time saving of 14 s per injection are proving promising.

Reduction in sampling time really needs to be considered in the design of the complete ETAAS system, as Varian have done in their recently launched Spectraa 600 and 800 series spectrometer systems. Sample and modifier pipetting are carried out while the furnace programme is running and injection is made into the tube about 12 s after the end of the heating programme. The smaller mass of graphite in the Varian furnace presumably cools more quickly than the Perkin-Elmer furnace used in the work described above. Using this new system, Shrader *et al.*[67] demonstrated that it is now possible to achieve cycle times of 36–47 s in the determination of cadmium in water, wine, beer and human serum samples. Perkin-Elmer

Table 4 Applications of fast furnace analysis

Element(s)	Matrix	Ashing stage	Comments	Ref.
Ag, As, Cd, Cr, Cu, Ni, Pb	Food, plant, water, sediment and urine RMs	No	Samples (except water) digested before analysis	49
Al	Dialysate fluids	Yes	Combined dry/ash stage	55
Al, Cu and Pb	Waters	No	Hot injection	35
Al, Fe	Bone, soft tissues	No	Samples digested with HNO_3	56
Al, Pb	Waters	No	High temperature drying, La modifier for Pb	48
As, Pb, Sr, Tl	Coal, fly ash	No	Slurries in 5% HNO_3, 0.04% Triton X-100. Problems with Se detection	53
As, Cd, Cu, Cr, Pb, Se, Ti and V	Plant, water, sediment, sewage sludge and urine RMs	No (except As and Pb in urine, As in sediment)	Hot injection onto a transversely heated graphite tube. Solid samples acid digested	57
As, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn	Soil, sediment, plant RMs, seawater	No (except Pb in seawater)	Slurries in dilute HNO_3 or digests with HNO_3–HF. Seawater analysed directly for Cd and Pb	54
Bi, Cu, Fe, Ni, Pb, Se, Te, Zn	Fine silver	No	High temperature drying. Matrix-matched standards. Samples dissolved in HNO_3	58
Cd	Blood	Yes	Samples deproteinized	32
Cd, Cr	Urine	Yes	Hot injection. Ammonium oxalate modifier for Cd	34
Cr, Cu, Pb	Plant materials	No (Cr, Cu) Yes (Pb)	$NH_4H_2PO_4$ modifier for Pb	33
Cr	Urine	No		52
Cr	Water	Yes	Cr speciated by extraction with APDC into IBMK. Combined dry/ash stage in slow ramp up to 900°C	59
Cr, Cu and Ni	Water	Yes	Hot injection	34
Cu, Cr and Pb	Diatomaceous earths	No	Slurries in 3% HF, high temperature drying, no clean stage	51
Cu, Cr, Co, Fe, Mn and Ni	Glasses	No	Slurries in 3% HF	60
Cu	Serum	Yes	Hot injection, anti-foam agent used	34
Cu	Serum	Yes		2
Cu, Cr, Fe, Pb and Zn	Sweets, chewing gum	No	Samples calcined at 400 °C prior to preparation of slurry from residue. High temperature drying	61
Cu	Urine	No		32
Cu, Fe, Ni and Pb	Urine, milk powder and bovine liver RMs	Yes	Pd modifier with H_2, hot injection. Milk and liver digested before analysis	36
Pb	Blood	No	Samples deproteinized	32, 62
Pb	Blood	Yes	$NH_4H_2PO_4$-HNO_3-Triton X-100 modifier	63
Pb	Soils	No	High temperature (400°C) drying	50
Pb	Teeth	No	Teeth digested in HNO_3	64

Table 5 Times taken by some commercial autosamplers in ETAAS, measured from the completion of the heating programme to the start of the programme after injection

Manufacturer	Model	Time/s
Perkin-Elmer	AS1*	29
	AS40*	29
	Zeeman 3030/AS60 (original software)	51
	Zeeman 3030/AS60 (revised software)	41
	1100/AS70	43
Varian	Spectra 30/40 with blank	38–42
	Spectra 30/40 without blank	33

* Early autosamplers with their own controller. Times are therefore independent of the spectrometer they are connected to.

have also recently introduced an autosampler, the AS-72, which allows preparation of samples while the furnace heating programme is proceeding.

Comparison With Other Techniques

Most of the AA spectrometers sold are single element instruments; multi-element AA spectrometers have still to make an impact. Fortunately there is still a demand for single element analyses. In the author's laboratory, most of the requests for trace element analysis require a single element, for example, the determination of blood lead for assessment of lead exposure under the UK Control of Lead at Work Regulations. However, the cost of ICP emission spectrometers and mass spectrometers is falling and where there is a need for multielement analyses, these techniques offer advantage of time and cost (particularly the cost of analyst's time) when compared with sequential single element analyses by AAS. The cost of an ICP emission spectrometer now approaches that of a complete graphite furnace AA system and recent developments with axial plasma viewing bring detection limits of commercial instruments close to those of ETAAS.[68] In the author's laboratory, a fast sequential ICP spectrometer with a vertically-orientated plasma has taken over much of the workload formally carried out by ETAAS and FAAS. It was first applied to the determination of aluminium and calcium in tap and purified water used in dialysis machines and replaced sequential determination by fast furnace AAS and FAAS for Al and Ca, respectively. Then a method for the determination for Al in serum was developed which, although often working close to the detection limit, has proved reliable and robust in the monitoring of serum aluminium in patients on dialysis, which brings in around 4000 samples per year. These methods[69] have given our laboratory good performance in external quality assessment schemes. Zinc and copper in serum and magnesium in urine are also now determined by ICP-AES, replacing determinations by FAAS.

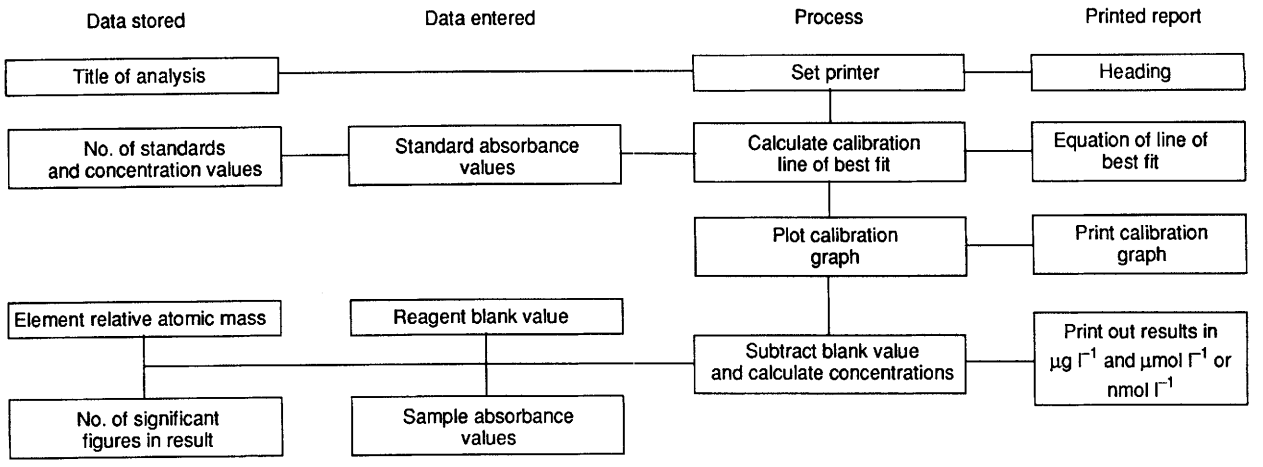

Fig. 2 Flow chart for computer programs for evaluation of analytical data customized for particular determinations

Electrothermal AAS is therefore likely to suffer intense competition from these alternative techniques. It seems reasonable to suppose that its future can be predicted from what has happened to FAAS. Flame atomic absorption spectrometers today are relatively simple and compact and have a market as low-cost analysers to laboratories with relatively simple analytical needs (*i.e.*, the analysis of a few elements). To occupy a similar niche for the determination of elements at lower concentrations, ETAAS needs to be of lower cost than its competitors, relatively simple and fast enough to offer a comparable rate of analysis. Developments in fast furnace analysis have shown that ETAAS does not need to be as complex as conventionally practised. Indeed, the work by Slavin and co-workers[49,53,57] demonstrating that, for a large number of different determinations, modifiers and ashing stages are unnecessary leads to considerable simplification of the technique. Further evaluation and development are necessary, but the evolution of a simpler set of rules for temperature programming in ETAAS would be a step forward.

Evaluation of Results

This should follow the same concept in reducing the number of steps and time in the evaluation of results to a minimum. Computer software should enable the production of a calibration graph from the absorbance measurements of the standards and evaluation of results from the data for the samples. In the field of trace elements in clinical chemistry, it is often useful to know results in two sets of units, $g\,l^{-1}$ and $mol\,l^{-1}$. Standards and reference material data are frequently in $g\,l^{-1}$ units whereas in the UK, $mol\,l^{-1}$ units have been adopted as standard for the reporting of results in clinical chemistry. To obtain results in two sets of units in the same computer program, the element has to be specified, as the relative atomic mass is required for conversion. From two fundamental programs using linear and quadratic least squares fit, respectively, for calibration, a number of variants have been written in Microsoft Quickbasic specifically for determinations that form a significant part of the workload of our laboratory. This customization allows fixed standard values to be incorporated, correction for blank values and results to be evaluated in the two sets of units (Fig. 2). The programme is tailored to follow the pattern of the worksheet so that key entries logically follow in order. For the analysis of solid samples after dissolution, *e.g.*, arsenic in hair, the masses can be entered to calculate concentrations in the original sample. Results and calibration data are automatically printed out.

CONCLUSIONS

Minimisation of the parameters, time, cost, sample volume, energy requirements, reagent consumption and waste production leads to analytical processes which are simple, rapid and efficient in use of resources.

There are further advantages to be gained which are not so immediately apparent. Trouble-shooting is quicker and easier and, since the processes are simpler, there is less to go wrong. As an example, blanks obtained in the partial digestion procedure[24] were lower than a more complete digestion using HNO_3–H_2O_2.[70] In fast furnace analysis, there are incidental advantages of increased tube lifetime and a decrease in time-dependent effects during the course of a batch of analysis such as drift, evaporation and contamination of samples.

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