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Flow Injection Systems for Directly Coupling On-line Digestions With Analytical Atomic Spectrometry

Part 1. Dissolution of Cocoa Under Stopped-flow, High-pressure Conditions*

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A double flow injection manifold incorporating a resistively heated oven is under development for the direct coupling of the digestion of solid samples with an analytical spectrometric technique. The potential of the system was illustrated by the dissolution of cocoa powder and subsequent determination of the copper and iron content by flame atomic absorption spectrometry (FAAS). The cocoa powder was slurried in 10% nitric acid, injected into the manifold and digested under stopped-flow, high-pressure conditions. Gas–liquid separation was effected by a two-stage de-pressurization system. Copper and iron were determined by flow injection FAAS against acid matched standards. Values of 44 ± 19 and 144 ± 10 mg kg^{-1} were obtained for the copper and iron content, respectively. The cocoa powder was also digested using an open-vessel hot-plate method and a closed-vessel microwave digestion method. The results for the copper content were 52 ± 2 and 50 ± 2 mg kg^{-1}, respectively. Both of these methods gave a value of 180 ± 10 mg kg^{-1} for iron. The relatively large uncertainty in the copper result for the on-line method was owing to the higher dilution in this system producing a concentration in the digest nearer the detection limit of the flame procedure. The low results for iron were considered to be owing to incomplete digestion, as agreement with the results of the other methods was obtained if the solution was analysed by the standard additions method. The proposed procedure produces a clear solution, and allows increased sample throughput while minimizing sample contamination and decreasing sample and reagent consumption.

Keywords: *Flow injection atomic absorption spectrometry; slurry sampling; on-line digestion; copper and iron determination; cocoa analysis*

The development of procedures for analytical atomic spectrometry for dealing with solid samples has been a long-term research theme.[1,2] The most widely adopted approach in practice is to harness the favourable free energy characteristics of a dissolution reaction to produce a homogeneous solution of the sample.[3,4] These decomposition procedures are often time consuming, requiring large volumes of aggressive and expensive reagents, and are prone to systematic error resulting from contamination and volatilization and adsorption losses.

Two other approaches to the development of a solid sampling procedure have been studied. The first involves direct solid sample introduction *via* erosion (*e.g.*, by arc or spark discharges) or vaporization techniques (electrothermal or laser ablation).[5,6] Non-homogeneous discharge conditions, intricate sample machining and preparation and a lack of suitable calibration standards are the major disadvantages of this approach. The second approach, that of slurry nebulization, has been developed as a means of simplifying sample pre-treatment for those samples for which the preparation of a slurry or suspension is feasible. Aqueous slurries have been introduced directly into the spectrometer and analysed against homogeneous calibration standards.[7] Results are highly dependent on the preparation of a stable slurry[8] in which the size of the suspended solids is sufficiently small so as to mimic a homogeneous solution in the atom source. Slurry preparation can be labour intensive, and seldom is the comparison of the slurry sample with solution calibration standards appropriate,[9] with the possible exception of electrothermal atomic absorption spectrometry.[10]

Many of the disadvantages of sample dissolution can be overcome by automating sample preparation in an enclosed system through the use of flow technology. Flow injection (FI) procedures involving sample decomposition have been described. For example, it has been shown that the measurement of chemical oxygen demand (COD), in which organic components of the sample were oxidized by a solution of potassium dichromate in concentrated sulfuric acid at a temperature of 180 °C in the presence of a silver catalyst, was possible.[11] Although many aspects of sample pre-treatment have been adapted to an FI format,[12] only a limited number of methods of solid sample prepration have been developed.[13–17] Burguera *et al.*[14] have reported a method for the determination of copper, zinc and iron in whole blood by flame atomic absorption spectrometry (FAAS). Sample and reagent were injected simultaneously into an aqueous carrier passing through a microwave oven. Dilute reagent concentrations and limited sample loading were maintained to avoid disruption of the flow profile by evolved gases.

A procedure for the determination of zinc and cadmium in biological tissue has also been reported.[15] Digestions were carried out in batch mode using a microwave oven with automated sample removal and introduction to an FAA spectrometer. The feasibility of slurry manipulation in an FI manifold has recently been demonstrated[16] followed by a report for the on-line digestion of slurried samples.[17] Sewage sludge was digested while flowing through a recirculating loop within a microwave oven cavity. The resultant digest was cooled in an ice trap to promote condensation of the acid vapors, de-gassed and passed through an injection loop to allow for discrete sample introduction to an FAA spectrometer.

A sample digestion system that was rapid, minimized reagent and sample consumption, avoided analyte loss or contamination and which rapidly transferred the resulting digest into the spectrometer for measurement would have clear advantages over existing, methodology, especially if

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the system could be fully automated. Procedures based on flow techniques certainly have the potential for the full automation of a number of manipulations, that in the traditional mode of implementation, are labour intensive. The use of the poly(tetrafluoroethylene) (PTFE) open tubular reactors of typical flow procedures provides a contamination-free handling environment with minimum analyte loss. This paper describes an approach to the development of such a digestion system.

In the present study, a double FI system designed for the atomic spectrometric determination of trace elements in samples with predominantly organic matrices is described and evaluated. A discrete volume of the sample slurry is injected into the first system and transported in narrow-bore PTFE tubing, mixed with nitric acid solution and pressure digested, under stopped-flow conditions, in a resistively heated thermal oven. A two stage, dual column assembly allows controlled de-pressurization of the system and gas–liquid separation. A sub-sample of the resulting digest is injected into the second FI system which is directly coupled to the atomic spectrometer. The use of a second FI valve allows the decoupling of the digestion manifold from the sample introduction manifold so that each can be optimized independently. Determinations in the resulting solution were made against calibration standards matched only with respect to acid content. For the experiments reported here, cocoa powder was chosen as the matrix, FAAS as the method of quantification and copper and iron as the analytes. The choice of cocoa powder was not entirely arbitrary; this was the material used by Gorsuch[18] as the model matrix in definitive studies on recoveries of elements after various methods of destruction of the organic sample components. Cocoa powder is readily available in large amounts and is likely to be homogeneous with respect to trace element distributions.[18] It contains several types of organic material, including fat, that are resistant to wet oxidation and it readily forms slurries in water-based fluids.

Experimental

Apparatus

A Perkin-Elmer 1100B atomic absorption spectrometer, equipped with a Perkin-Elmer data coded copper hollow cathode lamp operated with deuterium background correction, was used for all determinations. Instrumental parameters are given in Table 1. The signals were recorded on an Epson LQ-850 printer, all measurements being expressed as peak height absorbance. Microwave digestions were carried out using a CEM MDS-81 microwave oven equipped with a pressure transducer (CEM) and lined 100 ml Teflon-PFA digestion vessels (CEM). The magnetron frequency was 2450 MHz with a maximum power output of 630 ± 70 W adjustable in 1% increments. The manifold used is shown in Fig. 1. An Ismatec MS-4 Reglo/8-100 variable speed, multichannel peristaltic pump was used

Table 1 Instrumental parameters for the determination of copper and iron in cocoa powder

Parameter	Copper	Iron
Wavelength/nm	324.8	248.3
Lamp current/mA	25	30
Spectral bandpass/nm	0.7	0.2
Acetylene flow rate/l min^{-1}	2.0	2.0
Air flow rate/l min^{-1}	8.0	8.0
Burner height (arbitrary units)	8	8
Integration time/s	3*	3*
Number of replicates	3*	3*

*Continuous mode; for FI the signal was updated every 0.1 s.

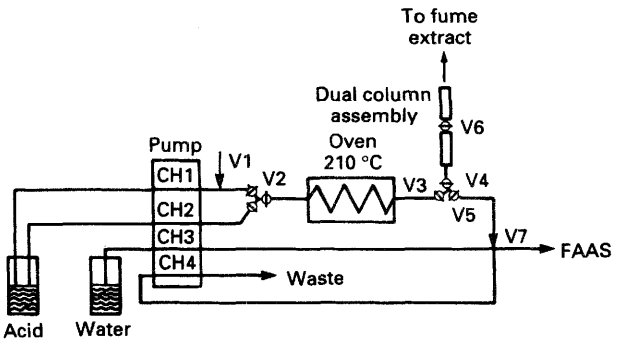

Fig. 1 Manifold for the stopped-flow digestion of slurry samples with an FI interface and FAA spectrometer: V=valve and CH=channel. For details of operation, see text

with Viton pump tubing (Cole-Parmer) and Technicon autoanalyser pump tubing.

The thermal oven was designed and constructed in the Department of Chemistry, Loughborough University, Leicestershire, UK, and modified to operate on 110 V line voltage. The heating elements were resistors of a few ohms mounted in an insulated box measuring 11 cm wide, 6 cm high and 3 cm deep. This oven was mounted on ceramic stand-offs above the box housing the power supply and control electronics. This box measured 12 cm wide, 7 cm high and 16 cm deep. A diagram of the oven and of the control circuitry is available on request from the authors. The oven contained 156 cm of 1.5 mm i.d. × 3.2 mm o.d. PTFE tubing (Omnifit). The tubing was wrapped in vertical coils around the resistive heating elements contained within the oven cavity. The remaining volume within the oven cavity was packed with fibre-glass insulation to reduce heat loss.

The valves used to contain the digesting sample were Omnifit Model 1103 three-way valves mounted upstream and downstream of the oven. The injection valves were six-port rotary valves with external loops (Rheodyne Model 50). The remaining manifold tubing consisted of 0.8 mm i.d. PTFE tubing. The collection column assembly consisted of two 10 cm, 6.6 mm bore Pyrex glass columns (Omnifit Model 436721) separated by a two-way valve (Omnifit Model 1101). All manifold channels were connected using high pressure gripper fittings (Omnifit).

Reagents

Analytical-reagent grade water produced by a Barnstead E-pure system was used for all solutions and as a carrier stream. Copper and iron standard solutions were prepared by dilution of standard solutions of the metal(II) nitrates (Fisher) containing 1000 mg l^{-1} of the metal. Digestions were carried out using nitric and sulfuric acids (both Fisher, analytical-reagent grade). The sample material was Hershey's cocoa powder batch number 76P. Triton X-100 (Sigma) as a 1% m/v solution was added to samples as required.

Procedures

Hot-plate digestion

The method used for the open-vessel hot-plate digestion of cocoa powder was modified from that described by Gorsuch[18] as follows.

A sample of cocoa powder (2 g) was accurately weighed into a clean Pyrex conical flask (500 ml). Concentrated sulfuric acid (10 ml) and concentrated nitric acid (15 ml) were added to the flask, which was covered with a watch-

Table 2 Optimum conditions for microwave digestion

Programme (stage)	Power (%)	Time/min
1	35	10
2	50	10
3	70	10

glass, placed on a cold hot-plate and the contents heated gradually to 230 °C. Successive 10 ml additions of concentrated nitric acid were made to the hot digest whenever the evolution of nitrogen dioxide fumes had ceased. The resultant solution was allowed to cool, then transferred into a calibrated flask (100 ml) and diluted to volume with analytical-reagent grade water.

Microwave digestion

The method developed for the closed-vessel microwave digestion of cocoa powder was as follows.

A sample of cocoa powder (0.5 g) was accurately weighed into a clean PFA–PTFE digestion vessel and concentrated nitric acid (5 ml) added. The vessel lid was hand-tightened and the carousel containing eight sample vessels was placed in the microwave oven. One vessel, used for pressure monitoring, was connected to the CEM pressure transducer *via* a water-filled pressure line. The contents of the vessels were heated according to the programme in Table 2. A peak internal pressure of 1.17 MPa (170 psi) was observed. The vessels were allowed to cool and the resultant solution was transferred into a calibrated flask (25 ml) and diluted to volume with analytical-reagent grade water.

Slurry preparation

A sample of cocoa powder (1.5 g) was accurately weighed into a clean 10 ml calibrated flask to which were added 6 ml of analytical-reagent grade water followed by 1 ml of concentrated nitric acid. The flask was shaken until the solid was homogeneously distributed, and the resulting slurry was diluted to volume with analytical-reagent grade water.

On-line digestion

All glassware was soaked in *aqua regia* [HCl–HNO_3 (3+1)] and rinsed in analytical-reagent grade water. The prepared slurry was transferred into a clean 10 ml beaker and constantly stirred with a magnetic stirrer to ensure homogeneity. The thermal oven was allowed to heat for 15 min prior to use. A slurry sample was injected into the manifold through valve (V) 1, with channel (CH) 1, CH2 and CH3 pumping at the designated flow rates (see Table 3). Valves 2, 3 and 5 were open, and V7 was in the load position. After 12 s, V2 and V3 were closed, and CH1 and CH2 were disengaged, trapping the slurried sample in the oven. After 3 min, V3 and V4 were opened (V5 and V6 closed) to allow for expansion of the pressurized digest into the first column with release of dissolved gases. After 1 min, V6 was opened slowly to allow for further de-pressurization of the digest into the second column. Valve 2 was then opened, and CH1 and CH2 were engaged until the digest was diluted to a known volume within the collection column. Valves 2 and 3 were closed and CH4 was engaged in order to pull the resulting digest from the column through the injection loop of V7, which was periodically switched to the inject position for the introduction of a discrete sample volume into the spectrometer. Typically, three injections were made for each digestion.

Table 3 FI parameters for the determination of copper and iron in cocoa powder

Parameter	Value
Injection volume, V1	174 μl
Injection volume, V7	329 μl
Oven volume	2.8 ml
Oven temperature	210 °C
Column volume	3.24 ml
CH1 flow rate	2.9 ml min^{-1}
CH2 flow rate	6.7 ml min^{-1}
CH3 flow rate	5.0 ml min^{-1}
CH4 flow rate	6.0 ml min^{-1}
Maximum oven pressure	3.45 MPa (500 psi)

After the determination was complete, a wash-out sequence was implemented as follows. Valves 2, 3, 4 and 6 were opened, V1 was in the inject position, V5 was closed, and CH1 and CH2 were engaged until the collection column was filled with concentrated nitric acid. Valves 2 and 3 were closed, V5 was opened, V7 was in the load position, CH1 and CH2 were disengaged and CH4 was engaged to pull the wash-out volume of acid from the column through the injection loop of V7.

Calibration was performed by detaching the manifold at V5, filling the injection loop of V7 with the appropriate calibration standard, and switching the valve to the inject position to introduce the standard into the spectrometer. As a possible method of simplifying the calibration procedure, a dual valve configuration as described by Carbonell *et al.*[17] was used. However, difficulties arose in matching the dispersion characteristics of the two valves.

Method Development

The possibility of direct nebulization of cocoa slurries either continuously or by FI introduction was studied as was the leaching of the elements into acid solutions. For the on-line digestion, the possible use of a single-line manifold was investigated, as was the viability of digestion in a continuously flowing stream. For the stopped-flow system, several ways of de-pressurizing the system, following digestion, and of gas–liquid separation were studied. These procedures included the use of a T-piece, microporous tubing, a single glass column (calibrated pipette) and a dual-column system. A variety of different slurries were prepared and evaluated for handling in an FI system. The slurry media investigated ranged from water to concentrated acids. The composition of the acid carrier was studied and the effect of different temperatures and stop times studied. Consideration was also given to the amount of material that could be injected and the volume of carrier needed to displace the digest from the oven. The accuracy of the sub-sampling of the slurry by the injection was assessed, as were the possible benefits of using Triton X-100 in the slurry preparation procedure.

Results and Discussion

Manifold Development

Preliminary experiments were conducted using a single-line continuous flow digestion manifold. The evolution and expansion of nitrogen oxides during the digestion process disrupted the flow profile within the manifold resulting in irreproducible residence times, uncontrolled dispersion and incomplete sample digestion. Gas–liquid separation and sample introduction into the spectrometer were also complicated by the pressure changes occurring within the manifold. Initial attempts at gas–liquid separation were

conducted using a glass T-piece. Difficulties were found with matching the flow rates of carrier flowing into and out of the T as a result of the constantly changing flow rate owing to gas evolution within the manifold. Consequently, sample loss was observed as a result of sporadic overflow of the top arm of the T.

The use of porous PTFE tubing to attain efficient degassing of the manifold was also considered. A 25 cm length of 0.5 mm i.d. Gore-tex tubing having a pore size of 2 μm was attached to the outlet of the manifold. A combination of the pressure increase owing to gas expansion within the manifold and the back-pressure of the small diameter tubing resulted in the acid carrier being forced through the walls of the porous tubing.

A third attempt at gas–liquid separation was made using a graduated pipette attached to a three-way valve for use as a collection column. This method provided efficient degassing of the carrier stream, a means of diluting the digest to a constant volume in order to ensure reproducible mixing and dilution, and a reservoir from which discrete volumes could be sampled and introduced into the spectrometer.

Digestions conducted in the continuous flow system were still incomplete as shown by the presence of particulate matter. For this reason, a stopped-flow, high-pressure system was developed (see Fig. 1). The graduated pipette was used as a collection column for de-pressurization of the system, gas–liquid separation and sample collection. Pressure release through the small orifice of the collection pipette resulted in aerosol formation and consequent loss of sample through the top of the pipette. The pipette was therefore replaced by the two stage column assembly shown in Fig. 1 to allow for a controlled dual stage de-pressurization of the manifold. On release of the pressure the flow of digest into the first column was controlled by the compression of the headspace vapours. When the flow had ceased, this headspace pressure was released by a controlled opening of the valve V6.

Slurry Composition

A number of different slurry compositions were investigated as shown in Table 4. Slurries in both water and hydrochloric acid proved to be stable and easy to manipulate. However, complete digestion of these slurries could not be achieved. In the single-line manifold, with injection of the slurry into the carrier of concentrated nitric acid, it was not possible to achieve complete oxidation without producing a large on-line dilution. Conversion to a double-line format with the introduction of a confluence point into the manifold, allowed the concentration of nitric acid across the sample profile to be increased. However, the slurry in water still failed to digest completely, and the rapid pressure increase associated with the hydrochloric acid slurry under these conditions prevented the digestion from proceeding for longer than 1 min without exceeding the pressure limits of the valves [3.45 MPa (500 psi)].

Cocoa slurries were then prepared in nitric acid by adding concentrated nitric acid in 1 ml increments to a 0.5 g sample of cocoa powder in order to determine the minimum volume of acid necessary to produce a slurry capable of being manipulated in an FI manifold. A 3 ml volume of acid was found to produce a slurry that could be pumped through 0.8 mm i.d. tubing. However, cocoa slurries prepared in concentrated nitric acid began to oxidize prior to introduction into the manifold. The evolution of gas from a partially digesting slurry made it difficult to dilute the material to a known volume. A slurry of 10% v/v nitric acid was found to be stable. In spite of the presence of nitric acid in the slurry, the use of a single-line manifold with a concentrated nitric acid carrier failed to provide adequate oxidizing power to decompose the sample. The final design was, as described above, based on a double-line manifold.

Some preliminary investigations into the direct determination of copper in various slurries by FAAS were conducted to determine if digestion of the particulate matter was necessary prior to analysis. Direct nebulization of the slurries resulted in immediate blockage of the nebulizer. The slurries were diluted by a factor of 30 and then introduced into the spectrometer both by direct nebulization and also by pumping through a single-line FI manifold with an analytical-reagent grade water carrier. In both instances, the copper concentrations determined to be present in the diluted slurry were low by approximately 40% compared with values obtained from procedures using hot-plate or microwave-oven digestion. The copper determinations were made against both aqueous and acid matched calibration standards. However, it was found that copper could be leached from the cocoa under relatively mild conditions and good recoveries could be obtained from the analysis of the supernatant after the material had settled. On the other hand, iron could not be determined accurately by this method. It was therefore considered that for multi-element determinations it would be necessary to digest the cocoa.

Study of Operating Parameters

The oven was maintained at its maximum temperature of 210 °C throughout the investigations to ensure the strongest possible oxidizing conditions. The composition of the carrier stream was initially 10% v/v sulfuric acid in concentrated nitric acid in an attempt to raise the boiling-point and therefore the oxidizing power of the carrier stream. Digestions carried out using carrier streams of 0, 10, 20, 30, 40 and 50% sulfuric acid in concentrated nitric acid demonstrated no effect on the quality of the digestion as shown by the clarity of the digest and lack of particulate matter. Digestions of the slurried sample were also attempted using both air and water as carrier stream. In both instances, digestion was observed to be incomplete. It was therefore concluded that a concentrated nitric acid carrier would be used in further investigations. The injection

Table 4 Slurry compositions investigated

Cocoa mass/g	Slurry medium	Final volume/ml	Comments
1.5	H_2O	10.0	Stable slurry
0.5	Concentrated H_2SO_4	10.0	Flocculated
0.5	Concentrated HCl	10.0	Stable slurry
0.5	Concentrated HNO_3	10.0	Digesting slurry
0.5	Concentrated HNO_3	1.0	Paste
0.5	Concentrated HNO_3	2.0	Sludge
0.5	Concentrated HNO_3	3.0	Digesting slurry
0.8	50% HNO_3	10.0	Digesting slurry
1.5	20% HNO_3	10.0	Digesting slurry
1.5	10% HNO_3	10.0	Stable slurry

volume was determined based on the dispersion of the manifold so that the dispersed sample zone could be completely trapped in the oven during the digestion. A 174 μl injection volume proved to be satisfactory for this purpose. The required residence time of the slurry in the oven was determined by performing a series of digestions at various residence times followed by evaluation of the resultant digest. A 3 min residence time was found to provide complete dissolution of the slurry. It was necessary for the volume of the collection column to exceed that of the oven in order to wash adequately the dissolved sample into the collection column, otherwise sample losses were observed.

Determination of Copper in Cocoa Powder

The on-line digestion procedure was validated by comparison of the results with those obtained from hot-plate and microwave digestions of the sample followed by the determination of copper by FAAS. The results of the determination are given in Table 5. Calibration data for the determinations are given in Table 6. A characteristic concentration of 0.088 mg l^{-1} was routinely achieved. A limit of detection ($3s$) of 0.065 mg l^{-1} in the digest and 7.9 mg kg^{-1} in the solid was calculated from the calibration graph.[19]

The larger uncertainty associated with the on-line digestion procedure arises mainly from the higher dilution in the on-line procedure. For the hot-plate and microwave procedures, the ratio of final volume of solution for analysis to initial sample mass is 50 ml g^{-1}. For the slurry, the 174 μl sub-sample injected introduces 26.1 mg of material into the manifold which is eventually diluted to 3.24 ml, giving a ratio of 124 ml g^{-1}. As the dilution arises from a number of distinct stages in the over-all operation, there is some scope for reducing this number and this is under study at present.

As a result of the large dilution factor, the solutions introduced into the spectrometer have copper concentrations (approximately 0.4 mg l^{-1}, depending on the mass of cocoa taken) within an order of magnitude of the detection limit[19] of the instrument (0.065 mg l^{-1}). Hence the uncertainty in the concentration interpolated from the calibration graph will be large. The over-all uncertainty is increased because of the need to subtract a substantial acid blank concentration, determined to be 0.21 mg l^{-1}. This source of uncertainty could be reduced by using a higher purity grade of acid.

Determination of Iron in Cocoa Powder

It had been demonstrated that copper could be leached from the cocoa by warm dilute acid, therefore, it was considered that the results for the determination of copper did not demonstrate that the sample matrix had been completely decomposed. However, as it had been shown that slurry nebulization did not give accurate values, it was clear that dissolution of the matrix had occurred. Results for the determination of iron were variable and sensitive to the fuel:oxidant ratio when an air–acetylene flame was used, suggesting that other components in the sample were causing vaporization interferences possibly because of incomplete decomposition.[20,21] Initial determinations gave rise to values of 144 ± 10 mg kg^{-1} for the FI procedure and 127 ± 10 mg kg^{-1} for the microwave procedure. Extensive investigation of the calibration procedure and optimization of the flame conditions produced agreement between the hot-plate and microwave methods at 180 ± 10 mg kg^{-1}. The FI values were consistently around 140 mg kg^{-1} when measured against matrix matched standards.

One possible reason for the apparent low recovery was considered to be the inadequacy of the sub-sampling of the slurry. The use of Triton X-100, to ensure homogeneous dispersion of the solid[10] and hence a representative sub-sample in the sample loop, did not improve the recovery. It was considered possible that solid material was lost while filling the loop, resulting in a more dilute slurry being injected than had been prepared. In order to test this hypothesis further, the loop was loaded and flushed directly into a microwave digestion vessel. After digestion in the microwave oven, the iron content was determined to be 170 ± 10 mg kg^{-1}, not significantly different from the values obtained by direct analysis *via* the hot-plate or microwave method. It was concluded that the matrix was not fully

Table 5 Results for the determination of copper and iron in cocoa powder

Parameter	Hot-plate	Microwave	On-line digestion
Number of replicates	6	5	13
Average copper concentration/ mg kg^{-1}	52.1 ± 2.3	50 ± 2.2	44 ± 19
Average iron concentration/ mg kg^{-1}	180 ± 10	180 ± 10	144 ± 10
Volume of nitric acid required/ml	100	5	8
Time/min	120	30	8

Table 6 Calibration data for determination of copper and iron in cocoa powder

Parameter	Hot-plate	Microwave	On-line digestion
Number of points:			
Copper	5	6	5
Iron	6	5	5
Slope/A l mg^{-1}			
Copper	3.989×10^{-2}	4.218×10^{-2}	3.162×10^{-2}
Iron	6.000×10^{-2}	6.151×10^{-2}	2.530×10^{-2}
Intercept/A:			
Copper	2.6415×10^{-3}	1.7136×10^{-3}	6.7912×10^{-3}
Iron	6.667×10^{-3}	6.837×10^{-3}	3.300×10^{-3}
Correlation coefficient:			
Copper	1.000	1.000	0.9990
Iron	0.9990	0.9995	1.000

decomposed by the FI procedure. This was further supported by results from the analysis of FI digests by the standard additions method for which results in agreement with the hot-plate procedure were obtained but for which the slope of the plot was decreased. Although it would be possible to implement an FI standard additions procedure[12] for the analysis, this was considered an undesirable direction to pursue for further development as the aim of the work is the removal of the matrix.

Further Developments

The present limitations of the digestion manifold would appear to be: (*i*) the incomplete decomposition of the matrix material; (*ii*) the high dilution factor resulting from the limited sample capacity of the on-line oven; and (*iii*) the need to achieve reliable de-pressurization and gas–liquid separation resulting in a solution the concentration of which is spatially homogeneous. It is noted that the microwave system apparently achieves a higher degree of matrix decomposition although the pressure does not rise above 1.17 MPa (170 psi). It is possible that the relatively large headspace in the microwave vessels allows gas evolution to proceed to a greater extent than occurs in the FI manifold which, in turn, allows the reaction to proceed further as the products are 'removed'.

The operating pressure of the FI system is currently limited to that of the weakest component in the system, which is probably the tubing. Although this should withstand pressures in excess of that to which the valves are rated [3.45 MPa (500 psi)], it is likely that the cycle of heating and pressurizing will steadily weaken the tubing located in the oven. It is considered necessary to be able to monitor pressure in the FI manifold so that: (*i*) further optimization can be made (*e.g.*, an examination of the role of the deliberate introduction of 'headspace' in the form of air bubbles); and (*ii*) a catastrophic failure of a manifold component owing to over-pressurization can be avoided.

An improved oven design is currently under consideration in an attempt to overcome some of these limitations. More efficient means of gas–liquid separation and manifold de-pressurization are also being investigated, as is the use of acids of higher purity in order to reduce the blank. Future investigations will consider other matrices and analytes and also the use of microwave heating for the digestion and either electrothermal atomic absorption spectrometry or plasma spectrometry as alternative, more sensitive, methods of measuring the trace elements in the resulting digest.

With respect to the time involved, it remains to be demonstrated that a fully developed and optimized FI or continuous flow based system would be more effective than a properly designed batch procedure. However, it is worth bearing in mind that the capacity of the present generation of microwave ovens for sample digestion is rather limited and that this and other types of pressure digestion often require long cooling periods before vessels can be opened. The digest still has to be quantitatively transferred into a calibrated flask and diluted to volume prior to analysis. It would be possible to improve the throughput of a flow system by the use of several lines in parallel.

Conclusion

The feasibility of on-line, high-pressure dissolution of a slurry sample, the organic matrix of which is resistant to wet oxidation, has been demonstrated. It has also been demonstrated that a flow manifold for such digestions can be coupled directly to an atomic spectrometer *via* a simple FI valve interface. The proposed procedure shows the advantages over batch procedures of low reagent and sample consumption, minimal sample contamination and high sample throughput. The manifold is amenable to automation and allows for the use of aqueous calibration standards.

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