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Derivative Flame Atomic Absorption Spectrometry and Its Application in Trace Analysis

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Flame atomic absorption spectrometry (FAAS) is an accepted and widely used method for the determination of trace elements in a great variety of samples. But its sensitivity doesn't meet the demands of trace and ultra-trace analysis for some samples. The derivative signal processing technique, with a very high capability for enhancing sensitivity, was developed for FAAS. The signal models of conventional FAAS are described. The equations of derivative signals are established for FAAS, flow injection atomic absorption spectrometry (FI-FAAS) and atom trapping flame atomic absorption spectrometry (AT-FAAS). The principle and performance of the derivative atomic absorption spectrometry are evaluated. The derivative technique based on determination of variation rate of signal intensity with time (dI/dt) is different from the derivative spectrophotometry (DS) based on determination of variation rate of signal intensity with wavelength (dI/dλ). Derivative flame atomic absorption spectrometry (DFAAS) has higher sensitivity, lower detection limits and better accuracy. It has been applied to the direct determination of trace elements without preconcentration. If the derivative technique was combined with several preconcentration techniques, the sensitivity would be enhanced further for ultra-trace analysis with good linearity. The applications of DFAAS are reviewed for trace element analysis in biological, pharmaceutical, environmental and food samples.

Keywords: Signal models, Derivative technique, Atomic absorption spectrometry, Analytical performance, Trace analysis

INTRODUCTION

Flame atomic absorption spectrometry (FAAS) is an accepted and widely used method for the determinations of micro elements in a great variety of samples and is recognized as the preferred method over flameless atomic absorption spectrometry. However, its sensitivity doesn't meet the demands of trace and ultra-trace analysis for some samples. Analysts have investigated ways to enhance the sensitivity of FAAS, most of which focus on the improvement and application of preconcentration techniques by using chemical and physical methods. All reported methods based on the measurement of signal intensity, with no breakthrough in this measurement technique.

Several series of papers have been published on the historic development, properties and limitations of derivative spectrophotometry (DS). Several publications on the theoretical aspects of DS and its use in chemical analysis, pharmaceutical analysis, food analysis, clinical analysis and other fields of application published since 1994 have been reviewed [1]. The derivative technique is based on the determination of the rate of variation in signal intensity with

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wavelength (dI/dλ). A new derivative technique based on the determination of the rate of variation in signal intensity over time (dI/dt) was developed by the Sun group in 1994 for atomic spectrometry including applications for FAAS, cold vapor atomic absorption spectrometry (CVAAS), flow injection-flame atomic absorption spectrometry (FI-FAAS), and atom trapping flame atomic absorption spectrometry (AT-FAAS) [2]. This derivative technique is different from derivative spectrophotometry (DS), and has been applied to determine trace elements in biological and environmental samples with a higher sensitivity than conventional AAS. The main purpose of this paper is to review the methodology and application of derivative flame atomic absorption spectrometry (D-FAAS).

SIGNAL MODELS

Characteristics of Atomic Absorption Signals

Atomic absorption signals are shown in Fig. 1. Conventional signal for atomic absorption spectrometry (AAS) is a curve of intensity vs. time. Signal for FAAS is similar to a square wave; and signal for FI-FAAS is similar to a pulse signal. Signal for AT-FAAS consists of a square wave and a pulse signal to be used for analysis. The derivative signal for D-FAAS consists of an up-peak and a down-peak corresponding to the up-side and down-side of conventional signal, respectively. The derivative signal for FI-FAAS consists of an up-peak and a down-peak with the end connected to the head. The derivative signal for AT-FAAS consists of the two derivative signals of FAAS and FI-FAAS.

Signal Models for FAAS

A relationship between signal intensity and time is obtained by measuring the intensity of the spectrometric signal over time with different concentrations of analyte. The conventional signal model was obtained by computer simulation of the relationship and expressed as [3]:

For up-side: $A_u = A_0 (1 - e^{-\frac{t^a}{b}})$

For platform: $A_p = A_0$

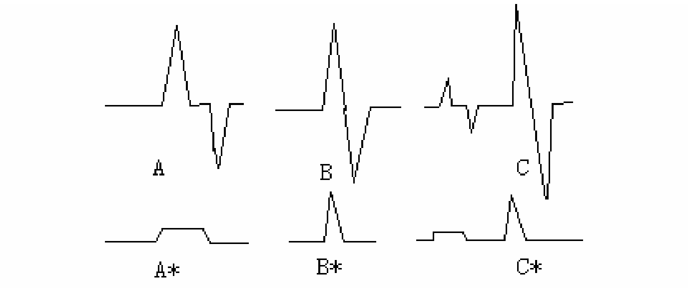

Fig. 1. Conventional and derivative signal of FAAS: (A*) FAAS, (B*) FI-FAAS, (C*) AT-FAAS, (A) D-FAAS, (B) D-FI-FAAS, (C) D-AT-FAAS.

For down-side: $A_d = A_0 e^{-\frac{t^c}{d}}$

The model for D-FAAS can be expressed as [4]:

For up-side: $dA_u/dt = \frac{a}{b} A_0 t^{a-1} e^{-\frac{t^a}{b}}$

For platform: $dA_p/dt = 0$

For down-side: $dA_d/dt = \frac{c}{d} A_0 t^{c-1} e^{-\frac{t^c}{b}}$

where A is the signal intensity (absorbance), A_0 is the maximum absorbance at which is dependent on the concentration of the analyte and *a, b, c,* and *d* are constants which are independent of the concentration of the same element over a greater range. For example, the values of *a*, *b, c,* and *d* are 1.73, 3.76, 1.37, and 2.16 for Cu and 1.49, 2.23, 1.46, and 2.31 for Co, respectively.

Signal Model for AT-FAAS and FI-FAAS

The signal model for AT-FAAS and FI-FAAS was obtained by computer simulation of the atomic absorption signal produced by injecting standard solutions of different concentrations, as follows [5]:

$$A = A_0 exp[-(\varepsilon t)^2/(\sigma + \delta t)]$$

Table 1. $\delta, \sigma,$ and ε for Cu, Zn , and Cd

Concentration	Cu for FI-FAAS			Zn for FI-FAAS			Concentration	Cd for AT-FAAS		
（mg l^{-1}）	δ	σ	ε	δ	σ	ε	（μg l^{-1}）	δ	σ	ε
1	0.453	35.7	0.479	0.535	18.16	0.32	0.05	0.6	28.3	0.31
2	0.453	35.6	0.481	0.538	18.11	0.32	0.10	0.6	26.8	0.33
3	0.454	35.6	0.481	0.533	18.51	0.31	0.15	0.7	26.6	0.34
4	0.454	35.7	0.479	0.535	18.41	0.32	0.20	0.6	27.3	0.31
Average	0.453	35.7	0.480	0.534	18.31	0.312	Average	0.6	27.3	0.32

where A_0 is the maximum absorbance and δ, σ and ε are parameters relating to analyte and experimental conditions, obtained by computer analysis of the experimental curve (A-t) for the standard solution at different concentrations (Table 1). δ, σ, and ε are constants for any element in a larger range of concentration.

The variation of signal intensity over time was obtained by derivating the model to time.

$$dA/dt = -A_0 \cdot exp[-(\varepsilon t)^2/(\sigma+\delta t)][\varepsilon^2 t(2\sigma+\delta t)/(\sigma+\delta t)^2]$$

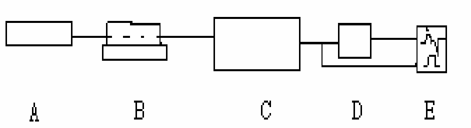

Fig. 2. Derivative atomic absorption spectrometric system. (A) Lamp-house, (B) Atomizer, (C) Spectrophotometer, (D) derivative measurement system, (E) Recorder.

PRINCIPLE AND PERFORMANCE

Derivative Analysis Principle

The laboratory-made derivative measurement system consists of a magnification and a differential unit. The output signal has a rigorous derivative relation with the input signals. The output signal of the system will stay within the baseline when the variation of the input signal is zero, and when the variation of the input signal is not zero, there is a corresponding polar output which is in direct relation to the variation of the input signal. The derivative system was connected between an atomic absorption spectrometer and a double-pen recorder, as shown in Fig. 2. The derivative and conventional signals were recorded simultaneously with the double-pen recorder.

Based on the differential principle, the intensity of the output signal of the derivative measurement system was expressed as $D = -m.B.RC.dA/dt$, where m is magnification factor of the magnification unit, RC is the time constant of the differential unit, B is the sensitivity of the differential unit. The height of the up-peak and the down-peak of the derivative signal are expressed as D_u and D_d, respectively. The equations for the up-peak and the down-peak of the derivative signal were obtained. The total height of the up-peak and the down-peak is expressed as:

D-FAAS

$$D = m.B.RC.\mathrm{A}_0 \left(\frac{a}{b}\mathrm{t}^{\mathrm{a-1}}\ e^{-\frac{t^a}{b}} + \frac{c}{d}\mathrm{t}^{\mathrm{c-1}}\ e^{-\frac{t^c}{d}}\right)$$

D-AT-FAAS

$$D = m.RC.B.A_o\, exp[-(\varepsilon t)\ ^2/(\sigma+\delta t)] \cdot [\varepsilon^2 t(2\sigma+\delta t)/(\sigma+\delta t)^2]$$

For the derivative system, both RC and m are constant. Because $A_0 = kc$ for FAAS, CVAAS, FI-FAAS and AT-FAAS, used the peak time as the measurement time, the intensity of the derivative signal can be expressed as $D = K.B.c$ ($K = k.m.RC$). When B was selected, the intensity of the derivative signal would be directly proportional to the concentration of the analyte. This provided theoretical principle for derivative atomic absorption spectrometry.

Analytical Performance

The curve drawn based on the mathematical model is in good agreement with the signal measured experimentally. For D-FAAS at 2 mV min^{-1} the sensitivities are 50 times higher than conventional FAAS, and the detection limits are also much lower, with a 10-fold improvement [6]. The use of the derivative technique combined with several preconcentration steps enhances the analytical sensitivity noticeably.

The derivative technique combined with an atom trapping method result in a 1000-fold improvement in sensitivity over conventional FAAS.Comparisons of the performance analyses for D-FAAS and conventional FAAS are shown in Table 2. It is indicated that the derivative signal processing technique has very high capability for enhancing sensitivity. D-FAAS has been applied for direct determination of trace elements without preconcentration. If the preconcentration methods published in the literatures [9-17] were combined with the derivative technique, the sensitivity would be enhanced further for ultra-trace analysis.

The test results have already proven that the derivative

Table 2. Improved Sensitivity and Detection Limits of FAAS with the Derivative and Preconcentration Techniques Compared to Conventional FAAS

Enhancing method	Element	Multiple for increased sensitivity	Ref.
D-FAAS	Cu, Pb, Cd, Mn, Fe, Zn	50 times	[6]
Enhancing effect D-FAAS	Cr	68 times	[7]
Solvent extraction -FAAS	Cu, Cd, Mg, Mn, Ag, Cr	75, 63, 74, 76, 74, and 130% for extraction with acetone; 35, 42, 43, 45, 50, and 140% for extraction with ethanol	[9]
Membrane separation -FAAS	Ag	82 times	[10]
Ion exchange -FAAS	Cd	8 times	[11]
Sulfhydryl cotton enrichment-FAAS	Cd	10 times	[12]
Cloud point extraction -FAAS	Mn	57.6 times	[13]
Flow injection on-line ion-exchange preconcentration -FAAS	Cu	23 times	[14]
Flow injection on-line double chelating resin column -FAAS	Cu, Pb, Cd, Mn	33, 50, 37 and 29 times, respectively.	[15]
Coprecipitation -FAAS	Cu, Ni	Concentration factors of 14.8 for Cu and 4.7 for Ni	[16]
Electrochemical minitype pond - FAAS	Cu	410 times	[17]
D-ATFAAS	Cu	2 orders	[18]
D-ATFAAS	Cd, Pb	783.9 times	[20] [21]

flame atomic spectrometry has good linearity for the determination of trace element, such as Cu. Fe, Zn, Cu, Mn, Cd, and Pb [3]. The derivative flame atomic spectrometric methods that have combined several preconcentration techniques also showed good linearity. Regression equations and correlation coefficients are shown in Table 3.

APPLICATION OF DERIVATIVE FAAS

Biological Analysis

The concentration of copper in whole blood samples from the human ear was determined by D-FAAS using microsample-injection with very higher sensitivity than conventional microsample-injection FAAS [2]. Using D-FAAS with a closed vessel microwave digestion-flow injection technique the concentrations of copper and iron in human hair were determined [8].

The AT-FAAS with derivative signal processing has been applied to the determination of cadmium and lead in urine [22]. With a 1 min collection time, the characteristic concentration was 0.028 μg l^{-1} for Cd and 1.4 μg l^{-1} for Pb, and the detection limits (3σ) were 0.02 μg l^{-1} for Cd and 0.27 μg l^{-1} for Pb. The

Table 3. Regression Equations and Correlation Coefficients

Method	Element	Sensitivity range (mV min^{-1})	Regression equation	Correlation coefficient	Linearity range	Ref.
D-AT-FAAS	Pb	2	$D = 4.8 \times 10^{-3} C - 0.00934$	0.9995	0-500 μg ml^{-1}	[25]
		5	$D = 1.99 \times 10^{-3} C + 0.00189$	0.9997	0-500 μg ml^{-1}	
		10	$D = 9.97 \times 10^{-4} C - 0.00117$	0.9998	0-500 μg ml^{-1}	
		20	$D = 5.04 \times 10^{-5} C - 0.00237$	0.9985	0-500 μg ml^{-1}	
	Cu	20	$D = 1.4 \times 10^{-3} C - 0.\ 0016$	0. 9992	0 ~ 500 μg l^{-1}	[18]
		10	$D = 2.6 \times 10^{-3} C + 0.\ 0117$	0. 9991	0 ~ 500 μg l^{-1}	
D-FI-FAAS	Cu	20	$D = 3.731 C - 0.0767$	0.9984		[3]
	Zn	20	$D = 16.32 C + 0.19$	0.9983		
On-line pre-concentration-D-FAAS	Cr(III)	2	$D = 0.\ 717 C - 0.575$	0. 9991	0 ~ 90 μg l^{-1}	[30]
	Cr(VI)	2	$D = 0.\ 579 C - 1.\ 64$	0. 9989	0 ~ 180 μg l^{-1}	
On-line pre-concentration-D- FI-FAAS	Cr	2	$D = 8.59 \times 10^{-3} C + 0.001$	0.996	0 ~ 90 μg l^{-1}	[29]
		5	$D = 3.26 \times 10^{-3} C + 0.002$	0.9997	0 ~ 90 μg l^{-1}	
		10	$D = 1.56 \times 10^{-3} C + 0.001$	0.9997	0 ~ 90 μg l^{-1}	

detection limit and the characteristic concentration of the proposed method were 2 and 3 orders of magnitude higher for the 1-3 min collection time than those of FAAS for Cd and Pb, respectively.

Analysis of Medicines

D-FAAS has been applied for the determination of trace elements in medicines. The concentrations of Fe, Zn, and Ca in Erkangning, a kind of Chinese medicine, were determined by D-FAAS with higher sensitivity, lower detection limits and better accuracy, than those of FAAS [23]. The concentrations of Fe, Zn, and Ca are 39.66, 6.816, and 12.00 μg ml^{-1}, respectively. This method was used to determine Cu, Zn, and Mn in the Chinese herb Ajiao [24]. D-FAAS combined with an atom trapping technique was proposed to determine Pb and Ag in Chinese herbs [25,26]. The derivative method had detection limits and sensitivities that were, respectively, 1 and 2 orders of magnitude higher than those of FAAS.

This method has also been used to determine trace zinc in Chinese herbal medicines [27]. At 20 mV min^{-1}, the characteristic concentration of 0.037 ng ml^{-1} was obtained for a 5 min collection, which was over 1000 times better than that of conventional FAAS. In order to simplify the equipment and operation, the atom trapping equipment was modified. This method was applied to determine copper in Chinese herbs by D-FAAS [18]. The characteristic concentration and detection limit for Cu were 0.85 and 0.52 μg l^{-1}, respectively, for a 10 mV min^{-1} sensitivity range setting and 2 min collection time, which was enhanced by 2 and 1 orders of magnitude compared to conventional FAAS. The concentration of trace copper in several Chinese herbs was determined with a recovery of 94.2%-104%. Kang *et al.* have applied a micro slurry sampling technique combined with the derivative technique for the determination of trace Cu, Fe, and Zn in Chinese herbal medicines with detection limits of 0.019, 0.058 and 0.013 μg ml^{-1} and relative standard deviations (RSDs) of 3.2, 3.9, and 4.2%, respectively [28].

Environmental Analysis

The determination of trace elements has received increasing attention in environmental pollution studies. In particular, there is an increasing need for a simple, sensitive and accurate method for determining sub -parts-per-billion levels of elements in environmental waters.

Ion-exchange on-line preconcentration was used to determine cadmium in environmental water samples with RSDs of 2.8-4.2% [11]. The sensitivity was enhanced by 8 times and 35 times higher than those of FAAS using sampling frequencies of 30 h^{-1} and 8 h^{-1}, respectively. It has been reported that the sensitivities for the determination of Cu, Mn, Fe, Zn, Cd, and Pb by D-FAAS are remarkably improved over those of FAAS by 20-50 times [6]. In addition, the detection limits are in the range of 5 to 11 times lower. This method has been applied to water analysis with recoveries in the range of 90.0-110.0%.

A rapid and sensitive method has been developed for the sequential determination of Cr(III) and total chromium in water samples by flow injection D-FAAS using on-line preconcentration with a double-microcolumn system [29]. The Cr(III) in samples without a reducing agent and total chromium after appropriate reduction of Cr(VI) to Cr(III) were respectively retained on two microcolumns containing cation exchange resin and were eluted directly into a nebulizer using 3 mol l^{-1} HNO_3. The characteristic concentration and the detection limit (3σ) for chromium were 0.535 μg l^{-1} and 1.09 μg l^{-1}, respectively. The proposed method allows for the determination of chromium in the range 10-90 μg l^{-1} with a relative standard deviation of 3.63% at a rate of 60 samples h^{-1}. This method has been applied to the analysis of chromium in water reference material (GBW08607) and other water samples with satisfactory results.

A new method has been developed for the sequential determination of Cr(III) and Cr(VI) in water samples based on flow injection on-line preconcentration and separation using a two-microcolumn system D-FAAS [30]. The Cr(III) and Cr(VI) in water samples were respectively retained on two microcolumns, one containing cation exchange resin and the other containing anion exchange resin, and were then eluted directly into nebulizer with 15% HNO_3 and 8% NH_4NO_3. The characteristic concentrations for Cr(III) and Cr(VI) at a sensitivity grade of 2 mV min^{-1} for a preconcentration time of 1 min were 0.130 μg l^{-1} and 0.0985 μgl^{-1}, which were 332 and 431-fold better than those of FAAS, and 45- and 47-fold better than those of FI-FAAS, respectively, The relative standard deviations were 4.27% and 3.66% and the corresponding detection limits (3σ) were 0.244 μg l^{-1} and 0.235 μg l^{-1}.

Satisfactory recoveries in the range of 94.40%-106.3% could be obtained from the water samples.

The species of Cr(III) and Cr(VI) in water samples were determined by flow injection on-line preconcentration and separation on two-microcolumn system D-FAAS during a collaborative analysis for certification [31]. The Cr(III) and Cr(VI) in water samples were retained on two microcolumns with ion exchange resin and were eluted directly into a nebulizer by 15% HNO_3 and 8% NH_4NO_3, respectively. The characteristic concentration (with a the sensitivity grade of 2 mV min^{-1} and a one min preconcentration time) for Cr(III) and Cr(VI) were 0.130 and 0.0985 μg l^{-1}, 332- and 431-fold better than those of FAAS, and 45- and 47-fold better than those of FI-FAAS, respectively.

The (RSDs) were 3.27% and 3.66% with corresponding detection limits (3δ) of 0.244 and 0.235 μg l^{-1}, respectively. The linear ranges of determinations for Cr(III) and Cr(VI) were 0-100 μg ml^{-1} with correlation coefficients of 0.9984 to 0.9996. Satisfactory recoveries in the range of 94.4%-106% for Cr(III) and Cr(VI) were obtained from water samples.

The D-FAAS combined with the atom trapping technique has been applied to the direct determination of trace lead in water and liqueur [32], and silver and cadmium at parts-per-billion (ppb) in water [33,34]. The ion-exchange microcolumn-preconcentration D-FAAS was described for the determination of copper, iron and zinc in tap water with sensitivities of 0.29, 0.59, and 0.06 μg l^{-1}, respectively. The recovery and the RSD ranges of the proposed method were 91.13%-101.34% and 1.95%-4.28%, respectively. The detection limits for each metal were found to be 1.28, 5.85, and 0.68 μg l^{-1}, respectively [19]. The concentrations of zinc, copper and cadmium in compost and leachate were determined by D-FAAS using closed-vessel microwave digestion with RSDs of 2.1-3.2% [35]. The conditions of separation and enrichment for trace silver were studied. A new liquid membrane system of TOA-N 205-Kero sine-$NH_3 \cdot H_2O$ was setup and optimized. Recoveries over 98% and an enrichment of 82-fold were obtained. Ag^+ at ng ml^{-1} levels could be determined by FAAS. The method was applied to the enrichment of trace silver in geological samples with satisfactory results and an RDS of 2.4% (n = 10) [10].

Zhao *et al.* have applied the atom trapping D-FAAS developed by the Sun group for the determination of trace cadmium in fly-ash. The feasibility of the method was certified by determining trace cadmium in standard fly-ash (GBW08401 and 82201). Its sensitivity and detection limit were improved by 2-3 orders of magnitude and 1-2 orders of magnitude than those of conventional FAAS with 1-3 min collection time, respectively. The relative deviation was 6.25%-7.23% [36]. Feng *et al.* applied the atom trapping-derivative atomic absorption spectrometric method for determining cadmium and lead in fly-ash [20,21]. The sensitivity and detection limit of cadmium for 1 min collection time were improved 896 and 125 times better than those of traditional FAAS, and 77.8 and 37 times better than those of AT-FAAS, respectively. The sensitivity and detection limits for lead with a 3 min collection time were 783.9 and 104 times better than those of traditional FAAS with an RSD (n =10) of 5.3%.

An electrochemical minitype pond was applied to FAAS for determination of copper. The sensitivity and detection limits were enhanced by 410 and 160 times compared to that of conventional FAAS when 50 ml of solution was preconcentrated [17]. Used the derivative technique combined with the electrochemical preconcentration method, the measurement sensitivity would be obtained for ultra-trace analysis.

Food Analysis

A derivative atomic absorption spectrometric method with an atom trapping technique was described for the determination of cadmium in flour [37]. The detection limit and sensitivity of the proposed method were improved by two and three orders of magnitude over those of conventional FAAS with a 1-3 min collection time. The characteristic concentration and detection limit (3σ) for cadmium were 0.027 and 0.019 μg l^{-1}, respectively, for a 1 min collection time and a 10 mV min^{-1} sensitivity range. The proposed method was applied to the determination of cadmium in flour samples with a recovery range of 94.7-119%. This method was also applied to determination of cadmium in vegetables with a characteristic concentration and detection limit of 0.026 μg l^{-1} and 0.02 μg l^{-1}, respectively, for a 1 min collection time and a 2 mV min^{-1} sensitivity grade [38]. Ji *et al.* applied DFAAS using a micro-suspension sample injection for determining copper, iron and zinc in maize flour [39].

A new method based on the technique of closed vessel microwave digestion and DFAAS was presented for the determination of iron and zinc in milk powder. The sensitivities of the method for Fe and Zn were 18 times and 8 times higher, respectively, than those of FAAS [40].

A flow injection approach for the preconcentration of copper and nickel from caustic soda by coprecipitation with $Fe(OH)_3$ was proposed. With sampling frequencies of 30 h^{-1} and 60 h^{-1} for copper and nickel respectively, concentration factors of 14.8 and 4.7 were only achieved with RSDs of 6.2% and 3.2%, respectively. The detection limits were 5.0 ng ml^{-1} and 60 ng ml^{-1} for copper and nickel, respectively [16]. The FI-D-FAAS has been applied to the determination of trace Ni, Mn, Cr, and Pb in vegetable oils [41]. The sensitivities for Ni, Mn, Cr, and Pb were 0.0054, 0.0034, 0.0067, and 0.052 µg ml^{-1} with RSDs of 0.3-2.8%.

A method for the determination of Mn in oil-bearing crops by D-FAAS with a trace injection technique was described [42]. The injection volume was 20 µl, the characteristic concentration, detection limit and RSD were 0.011 mg l^{-1}, 0.07% and 3.7%, respectively. The concentration of Mn in peanuts, black sesame and sunflower seeds were 0.12, 0.07, 0.12 and 0.64 µg g^{-1}, respectively.

The concentrations of zinc and cooper in milk powder and fish samples were determined by closed vessel microwave digestion and D-FAAS [43,44]. The D-FAAS technique with microsample-injection has been used to determine zinc in vegetable oils and copper in dairy products and several fruit juices [45-47].

Other Analysis

A new method for the determination of trace lead in copper is proposed by enhancing effect-flame atomic absorption spectrometry using a derivative technique [48]. The enhancing effect of matrix Cu on lead was investigated. The sensitivity for lead was enhanced 17 times over that of conventional FAAS by combining a derivative technique with the matrix Cu enhancing effect. This method was satisfactory with a 0.007µg ml^{-1} detection limit and a 0.7% RSD. A new method for the determination of trace chromium in copper and cooper-alloy was proposed using the enhancing effect-D-FAAS [7]. The enhancing effect of sodium dodecyl sulfate on chromium was investigated. The sensitivity for chromium was enhanced 68-fold over that of conventional FAAS by combining a derivative technique with the matrix Cu enhancing effect. D-FAAS was used to determine micro amounts of silver in copper [49]. The sensitivity of the derivative method was 21 times higher than that of FAAS. The detection limit was 0.0017 µg ml^{-1} (RSD 0.24%) with satisfactory accuracy and sensitivity.

CONCLUSION

The sensitivity of FAAS is limited by several factors. Although flameless AAS is a more sensitive technique than FAAS, this technique is more expensive, slower and more prone to interferences. It also requires expert operators. The derivative technique enhances the sensitivity of FAAS greatly. D-FAAS has been applied for the direct determination of trace elements without preconcentration. If a preconcentration method is combined with the derivative technique, the sensitivity would be enhanced further for ultra-trace analysis. D-FAAS plays an important role in analytical chemistry. The spectrum obtained with the derivative technique offers a convenient solution to the lower sensitivity of FAAS. Interesting applications will be found for the derivative signal processing technique in various fields of analytical chemistry.

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