

SIMULTANEOUS MULTI-ELEMENT ATOMIC ABSORPTION SYSTEM USING PHOTODIODE ARRAY DETECTOR

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ABSTRACT

A photodiode array (PDA) detector - multichannel analyser (MCA) system has been coupled to a flame and a graphite furnace atomiser and tested for simultaneous multielement atomic absorption analysis. Multielement hollow cathode lamps (HCL) are used as light source. Spectral lines are dispersed through a spectrograph with triple gratings and detected by a 25.4 mm PDA detector consisting of 1024 elements. The optical MCA system is capable of recording multiple spectra spanned by the spectrograph/PDA. The transmitted intensity spectra obtained for the standard and analyte solutions during flame or graphite furnace atomisation are converted to absorbance spectra using the MCA software provided. Results from the comparison studies show that the linear range and sensitivities for Ni-Co-Fe and Cu-Cr obtained from the simultaneous measurements are within the same order of magnitudes as those from conventional single element determinations using photomultiplier tube detection. The study also shows that non-atomic absorption can be readily corrected by a two-line method where non-atomic absorption lines can be chosen from the spectra recorded simultaneously. The proposed system has been evaluated for the determination of trace elements using NBS standard reference water SRM 1643b.

ABSTRAK

Suatu pengesan array fotodiod (PDA) dengan penganalisis multichannel (MCA) telah dipersatukan dengan pengatom nyala dan pengatom relau grafit. Sistem ini telah diujikan untuk analisis penyerapan atom multiunsur serentak. Lampu katod geronggang digunakan sebagai punca sinaran. Penyerapan garis spektra adalah dicapai melalui sebuah spektrograf yang dilengkapi dengan tiga buah parutan. Luas pengesan PDA ialah 25.4 mm dan jumlah unit unsur pengesan ialah 1024. Spektrum spektrum multipel selepas menerusi spektrograf/PDA boleh dirakam dengan menggunakan sistem MCA beroptik untuk larutan-larutan piawai atau sampel bagi analisis pengatoman dengan nyala atau dengan relau grafit.

Spektrum-spektrum penyerapan atom dihitungkan telah dibandingkan dengan butir-butir sama daripada instrumen penyerapan atom biasa yang menggunakan tiub pendarabfoto. Pengajian ini menunjukkan bahawa julat linear dan kepekaan untuk penentuan Ni-Co-Fe dan Cu-Cr serentak dengan menggunakan sistem baru ini adalah sebanding dengan penentuan menggunakan instrumen penyerapan atom biasa. Pembetulan untuk penyerapan bukan berasal atom mudah dijalankan dengan kaedah dwigarisan di mana garis penyerapan bukan berasal atom boleh didapati daripada sepktrum-spektrum yang telah dirakam. Penentuan unsur-unsur surihan dalam suatu sampel perujuk piawai daripada NBS (SRM 1643b) telah dijalankan untuk menguji kecekapan sistem baru ini.

INTRODUCTION

Atomic absorption spectrophotometry (AAS) with flame and graphite furnace atomisation developed since the late 1950's is the most widely used technique for trace and ultra-trace elemental analysis. It is well-known that the main limitation of both forms of AAS techniques is the single elemental nature in the measurements. This introduces serious drawbacks in terms of cost and per sample analysis efficiency. In the case of flame AAS, it also means that a relatively large volume of solution is required for the determinations of multi-elements in the sample. For graphite furnace AAS, the long injection-atomisation turnover cycle has seriously limited its applications despite being one of the most sensitive techniques in the medium cost range.

There have been numerous attempts to extend AAS for simultaneous multi-element detection. Basically the approaches can be differentiated in terms of the light source and the detection system used. Among these, most effort has been focussed on the continuum source atomic absorption spectrophotometry (CSAAS) since the detailed evaluation was reported by Fassel *et al.* (1966) for a system using a 150-W xenon arc lamp with a 0.5 m focal length monochromator and a photomultiplier for flame atomisation. Since then, various improvements, in particular, in the monochromator configurations, multiple photomultiplier tubes design and enhancement in source intensity and wavelength modulation have been progressed and tested (see reviews by Marshall *et al.*, 1986; O'Haver and Messman, 1986). Recently, Jones *et al.* (1989) reported a CSAAS in a graphite furnace with photodiode array detection which overcome some of the difficulties encountered in CSAAS such as the need for wavelength modulation and problems caused by spectral interferences. The biggest disadvantage is still the poor source intensity, especially below 250 nm. This has resulted in detection limits of 2-3 orders of magnitude higher than the best detection limits reported for commercially available line source graphite furnace

AAS for most elements.

In another category of approach, some research has been devoted to the adaptation of the instrumentation for multi-channel line source atomic absorption measurement (Pickford and Rossi, 1973; Lundberg and Johannson, 1976; Alder *et al.*, 1976; Salin and Ingle, 1978). This approach retains the advantage of the superiority in sensitivity and detection limits which can be achieved using atomic line source as against the continuum source. This type of systems, other than being limited in the choice of elements by the dependence on the multi-element hollow cathode lamps, generally lacks the capability for non-atomic background correction.

Commercialisation of simultaneous, multielement AAS instruments still appears to be not practical as there have been no significant breakthroughs to the inherent limitations of such systems. Two important considerations arising from the above assessment has led to the alternate design concept in this work. First, it is practically impossible for the continuum source approach to achieve the sensitivity and detection limits matching those based on the spectral line source method. Second, it is also recognised that dispersion optics and multi line detection instrumentation can be relatively simple if spectral line sources are used.

This work presents a simultaneous multi-element AAS system using photodiode array detector (PDA) and multi-element hollow cathode lamps as light source for both flame and graphite furnace atomic absorption analysis. The system allows rapid acquisition of multiple spectra of the wavelength region spanned by the PDA and absorbance spectra are calculated over the whole wavelength region. The system does not require any modulation in the light source and broad-band background absorption and spectral interference can be corrected directly in the spectra acquired. The linear range, sensitivity and detection limits of the system for flame and graphite furnace atomic absorption measurements are presented.

EXPERIMENTAL

Instrumentation. A schematic diagram of the instrumental arrangement used in this work is shown in Figure 1. The spectral line source is a multielement hollow cathode lamp containing Ni-Co-Fe-Mn-Cu-Cr (Photron Australia). The radiation from the lamp was focussed through the centre of the atomizer with a quartz lens. A Varian nebulizer and air-acetylene burner unit (Varian AA-4) has been adapted for flame atomisation while the graphite furnace atomiser employed was a Perkin Elmer Model HGA-300 instrument. Pyrolytically coated graphite tubes have been used in the graphite furnace studies. A second quartz lens at the exit end of the atomiser refocussed the beam to the entrance slit of the spectrograph (Jarrell-Ash Monospec-27) with three selectable gratings. Two of the gratings, with 2400 and 1200

grooves/mm and dispersion of 1.5 and 3.0 nm/mm respectively, were used in this study. The entrance slit width chosen was 50 μm ,

The dispersed light beam was directed towards the photodiode array detector (EG&G Model 1412) at the exit window of the spectrograph. The spectral and noise characteristics of the 1024 element self-scanned photodiode array detector have been reported by Talmi and Simpson (1980). As the detector controller (EG&G Model 1463) scans through all the diode element in serial, 1024 spectral intensity data point are obtained and stored in the detector interface (EG&G Model 1461) memory. The detector exposure or accumulation time for each spectrum can be set ranging from a minimum of 16 ms upwards. Multiple spectra can be accumulated at relatively short time intervals. The detector interface is equipped with a 68000 microprocessor and memory space of 320 kB which can store up to 50 spectra of 1024 data points each. At the end of the accumulation, the data were transferred to the host computer (Acer-910 80286-based microcomputer) for data analysis. The transmitted line intensity spectra obtained for both flame and graphite furnace AAS were processed using the OMA-88 software provided (EG&G, 1989). The absorbance of the spectral lines of the analyte elements was obtained as an integration of the absorption peaks in the absorbance spectra generated.

Sample Preparation. Stock spectroscopic solutions containing 1000 mg/L of the elements included in the study were obtained from BDH. A mixture of these elements was prepared and dilutions were made to obtain analytical calibration curves. An NBS standard reference water (SRM 1643b) has been used in the application test. Solutions containing a constant concentration of the test elements have also been prepared in NaCl matrix with concentration of NaCl ranging from 0.05% (w/v) to 4% (w/v) for evaluation of the capability of the proposed system for simultaneous correction of non-atomic absorption.

Procedure. The wavelengths of the principal atomic absorption lines of the five elements selected in the present study are listed in Table 1. At the beginning of the atomic absorption measurements, the spectrograph was set to cover the range of wavelength of the elements of interest. To cover the broad wavelength regions, two separate scan acquisitions were necessary. The higher resolution gratings (2400 grooves/mm) was used for the simultaneous determination of Co-Ni-Fe whereas a lower resolution gratings (1200 grooves/mm) was employed for Cu-Cr.

The background spectrum which is referred to as dark current and fixed pattern noise was first acquired by blocking the multielement HCL line source. This spectrum will be subtracted automatically by the OMA software from all transmitted spectra for the HCL line source detected by the PDA with or without aspirating or injected samples in the atomizer.

Simultaneous Multielement Flame AAS. Air-acetylene flame atomisation has been evaluated in this study. Optimum flame conditions and observation heights were established initially for the individual analyte elements. The simultaneous multielement flame AAS study employed conditions which are considered as optimum for all elements being studied. The transmitted line spectra through the flame atomiser were recorded as described above while aspirating the blank or analyte solutions into the flame. Spectra from the accumulation of 10 scans of 0.1 s exposure time each were used in the absorbance measurements.

Simultaneous Multielement GFAAS. The electrothermal graphite furnace operation involves four distinct pre-programmed time-temperature steps for drying, ashing, atomisation and cleaning. For the purpose of simultaneous multielement detection, the optimum ashing and atomisation temperatures used were based on the lowest ashing temperature and the highest atomisation temperature, respectively, established for the individual analyte elements of interest. For Ni-Co-Fe analysis, the following program steps were used:

STEP	TEMP, °C	RAMP, s	HOLD, s
1	120	10	20
2	800	20	40
3	2400	1	4
4	2400	0	3

Argon was used as the inert gas and gas flow was stopped during atomisation. Ten µl of the test solution were injected into the furnace in each run. The PDA was set to accumulate spectra of 10 scans each at 0.1 s exposure. The acquisition was initiated 7 s prior to the atomisation step and continued for 7 seconds. A total of 35 spectra was obtained for each injection-atomisation cycle. Determination of Ni-Co-Fe in SRM 1643b standard reference water of NIST was carried out by direct injection of 10 µL of the sample.

Two-Line Method for Non-Atomic Absorption Correction. The spectral lines span obtained by the PDA-OMA system can be utilised for background correction using non-atomic absorption lines from the HCL line source adjacent to the atomic lines of interest. The two-line method for non-atomic absorption background correction has been reported in literature. The non-atomic absorption lines adopted in this work were based on those recommended by Culver (1975), Fuller (1979) and Newstead *et al.* (1978) which are listed in Table 1.

Solutions with high solid content ranging from 1 to 4% NaCl were used in the study of the non-atomic absorption correction for Zn and Cu (tested at 1 ppm level) in flame AAS. For the electrothermal atomisation, solid contents ranging from 0.05% to 0.25% in terms of NaCl concentration were tested involving Ni, Co and Fe of 70 ppb each.

RESULTS AND DISCUSSION

Figures 2 and 3 show typical PDA spectra of multielement hollow cathode lamp line sources of Cu-Cr and Ni-Co-Fe, respectively. Resolutions of the gratings used were 0.068 nm/channel for Cu-Cr and 0.034 nm/channel for Ni-Co-Fe. The PDA scan covers a spectral range of 68 nm and 34 nm each through the two gratings. The wavelengths of the prominent lines of the elements of interest have been identified and coincide with those reported in literature. As shown, more than one major atomic absorption lines are normally available which are sufficiently well resolved for the atomic absorption measurements. The sensitivity and low spectral interference are therefore expected to equal those for conventional AAS. The added dimension of the new design is apparent in that atomic absorption spectra covers a given wavelength range can be acquired in a single measurement. Rapid acquisition of multiple spectra providing time-resolved information for the atomisation process is another enhanced feature of the system.

The simultaneous multielement capability is demonstrated in the flame atomic absorbance spectrum for a mixture of Ni-Co-Fe at 5 ppm (Figure 4). The strongest absorption peaks for Ni, Co and Fe at 232.00, 240.65 and 248.33 nm respectively are as expected based on the conventional AAS information. The relative absorptivities of the secondary absorption lines obtained from the spectrum as compared to the principal lines are approximately in the same order of magnitude as reported in literature.

Significant noise level is observed in the non-atomic continuum regions. This is to be expected since the emission intensity of the HCL in these regions is generally very low. The actual noise level at the atomic absorption lines is determined by the stability of the high intensity spectral lines from the HCL and the PDA detector noise. Low noise level comparable to the conventional AAS using photomultiplier detection, and hence the same detection limits, can be achieved by optimising the PDA detection exposure time and accumulation of multiple scans in the absorption measurements.

Figures 5a - 5c show the expanded time-resolved absorbance spectra for graphite furnace atomisation of Ni-Co-Fe at 70 ppb during atomisation in the various regions of interest. A 3-dimensional plot of Figure 5b for cobalt is shown in Figure 6 where the added time-resolved dimension is clearly demonstrated. The sequence of atomisation and disappearance of the analyte elements at the respective absorption wavelengths is captured. Useful information of the atomisation process can be retrieved from the recorded spectra. The overlay of absorption peaks at 252.33 nm in Figure 5c appears to indicate that there are two components making up the peak. Similar to the simultaneous multielement flame AAS, significant noise level is also apparent in the non-atomic continuum regions. However, much lower noise levels are seen in these Figures for the atomic absorption lines.

Calibration curves have been obtained for the evaluation of the sensitivity and linear range of the simultaneous multielement flame AAS and graphite furnace AAS system using photodiode array detection. Figure 7 shows the calibration curves for Cu-Cr standard mixture solutions by flame AAS. Calibration curves for Ni-Co-Fe by graphite furnace AAS are presented in Figure 8.

The specific performance in terms of the sensitivity, detection limits and the slope of the calibration curves is presented in Table 2 for flame AAS and in Table 3 for graphite furnace AAS. The sensitivities expressed as the concentrations giving an absorbance of 0.0044 units for the various elements tested in this study by flame AAS are two to three times higher than those reported for typical commercial instruments. Further improvement for the present system can be achieved with more systematic optimisation of the flame conditions and observation height.

Sensitivities for Ni, Co and Fe obtained from the present study for graphite furnace atomisation are about 2 to 4 times lower than those reported for commercial instruments. The capability of PDA system in rapidly acquiring multiple spectra during the furnace atomisation has contributed to the improvement in sensitivities.

Non-atomic absorption, in particular that arising from high solid content in the analyte solutions, can cause significant interference in the atomic absorption due to scattering of the atomic light beam by particulates formed during atomisation. Corrections for nonatomic absorption can be easily made by the two-line method using non-atomic absorption line of the element or an inert gas line which are recorded simultaneously in the PDA spectra. Results from the present study are presented in Figures 9 and 10 for flame and graphite furnace AAS, respectively. As observed, non-atomic absorption due to the presence of NaCl up to 4% (w/v) in flame AAS for Cu and Zn can be effectively corrected. In graphite furnace AAS, the two-line correction method is limited to a NaCl level of less than 0.3% for Ni-Co-Fe analysis.

The new system has been tested for the determination of Ni-Co-Fe in NBS (NIST) standard reference material (SRM 1643b water). The results obtained are consistent with the certified values within the limits of standard deviation.

CONCLUSION

We have designed a new simultaneous multielement AAS system using multielement hollow cathode lamp as light source and photodiode array detection. The system is suitable for both flame and graphite furnace atomisation. The very high level of sensitivity and other inherent advantages of conventional AAS such as freedom from spectral interference and the use of relatively simple optical system are inherited in the new design. The study shows that the new configuration offers, in addition, powerful features such as capability to acquire atomic absorbance spectra of a

complete wavelength region as well as time-resolved spectra at relatively short time intervals. Non-atomic absorption correction by the two-line method involving non-atomic absorption lines in the absorbance spectra can be readily made for both flame and graphite furnace atomisation without needs of any additional accessories.

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Table 1. Wavelength of spectral lines chosen for atomic absorption and non-atomic absorption measurements.

Element	Wavelength, nm (Atomic Absorption)	Wavelength, nm (Non-Atomic Absorption)
Cu	324.75	327.90
Cr	357.87	-
Ni	232.00	231.41
Fe	248.33	250.67
Co	240.72	238.83

Table 2. Performance of the multi-elemental simultaneous multielement flame AAS system.

Element	Wavelength, nm	Sensitivity*, ppm		Detection Limit, ppm	Calibration Gradient, ppm ⁻¹
		(This Work)	(Typical Literature)		
Ni	232.0	0.0843	0.040	0.0361	0.0425
Co	240.7	0.0808	0.040	0.0322	0.0397
Fe	248.3	0.0326	0.050	0.0321	0.0510
Cr	357.9	0.1476	0.040	0.0332	0.0202
Cu	324.8	0.0883	0.025	0.0255	0.0512

* Concentration giving an absorbance of 0.0044 units

Table 3. Performance of the new graphite furnace AAS with photodiode array for simultaneous determination of Ni, Co and Fe.

Element	Sensitivity*, ppb		Calibration Gradient ppb ⁻¹
	(This work)	(Literature)	
Ni	19	84	0.0073
Co	21	38	0.0143
Fe	9	20	0.0305

* Sensitivity defined as the amount injected to produce 0.0044 absorbance units.

Table 4. Simultaneous GFAAS determination of Ni, Co and Fe concentration in NBS SRM-1643b standard reference water.

Element	Certified, ppb	This Work, ppb
Ni	49.9	52.1 (±2.3)
Co	26.6	25.3 (±0.2)
Fe	99	100.5 (±2.6)

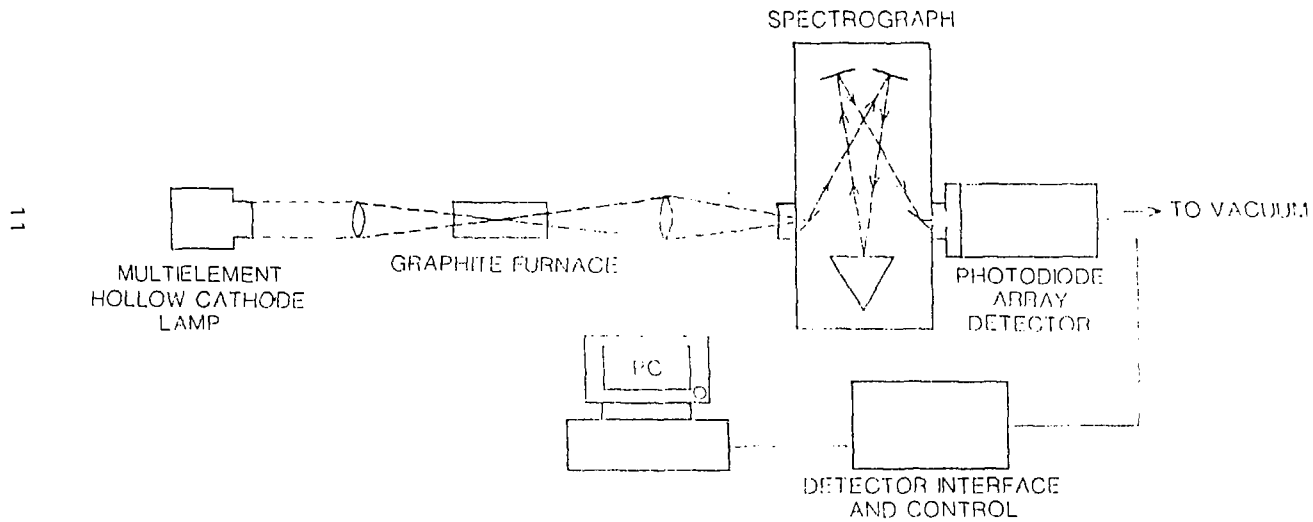


Figure1. Schematic diagram of the optical arrangement for the multi-element PDA - AAS system.

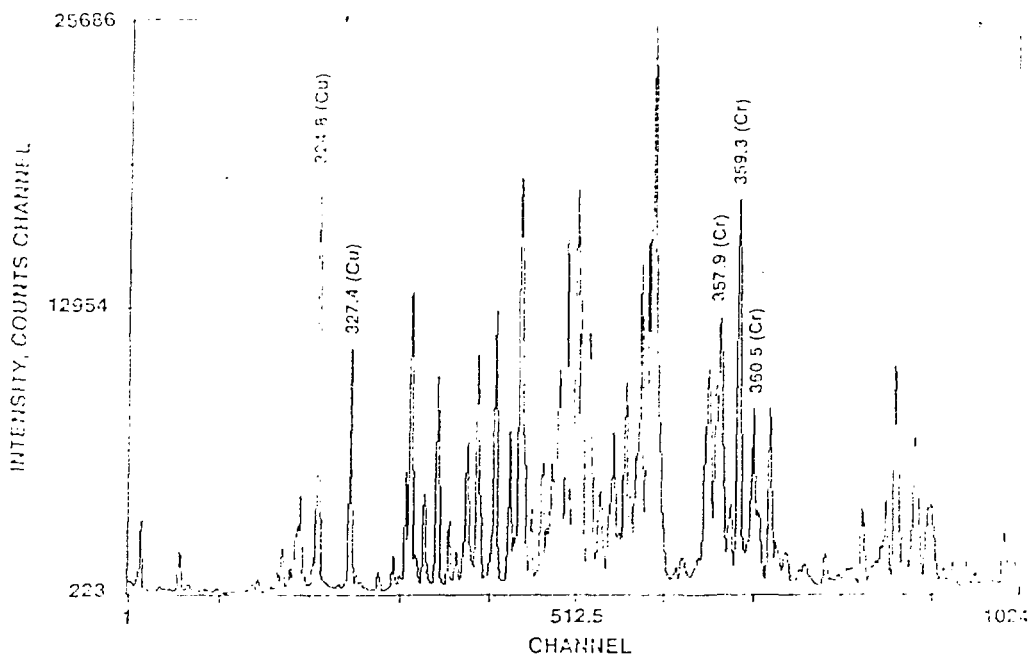


Figure 2. Spectrum of Cu-Cr hollow cathode lamp using photodiode array detector.

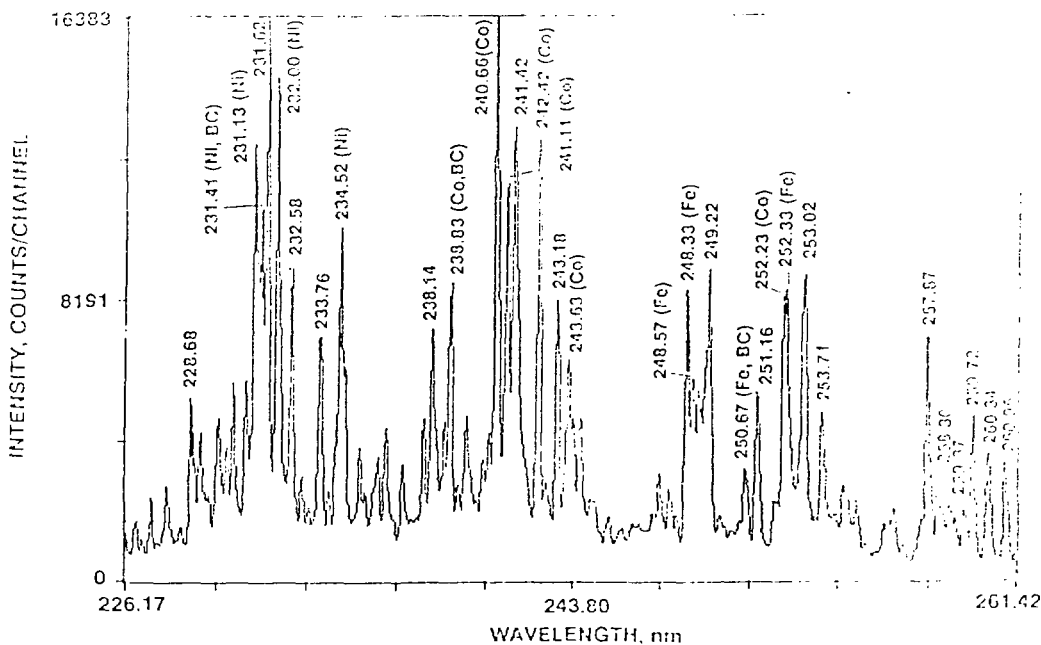


Figure 3. Spectrum of Ni-Co-Fe hollow cathode lamp using photodiode array detector.

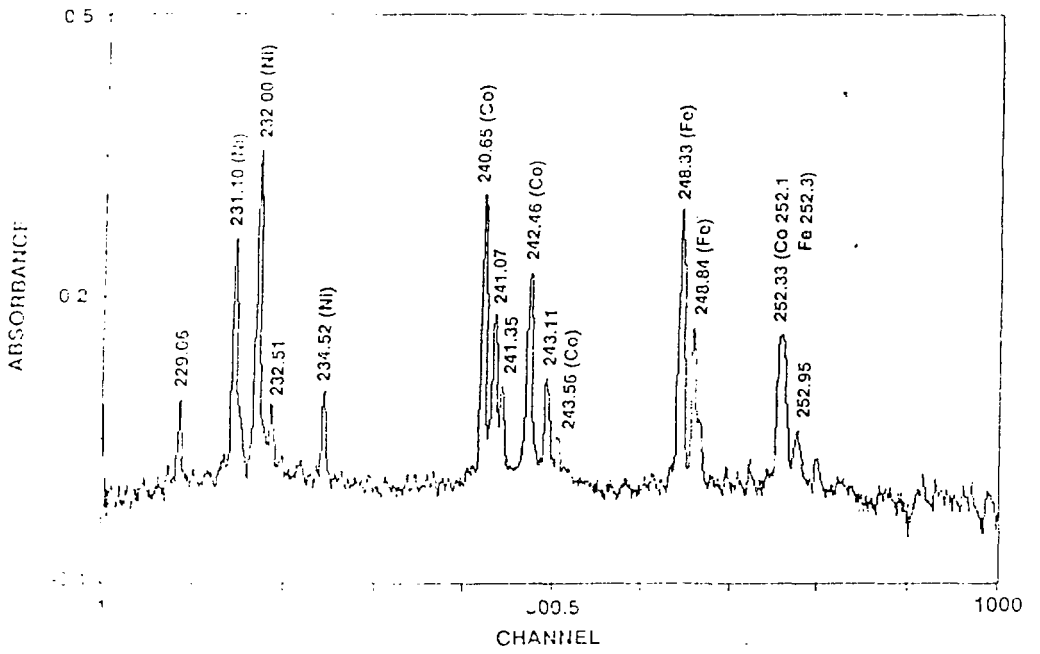


Figure 4. Absorbance spectrum of Ni-Co-Fe in flame AAS.

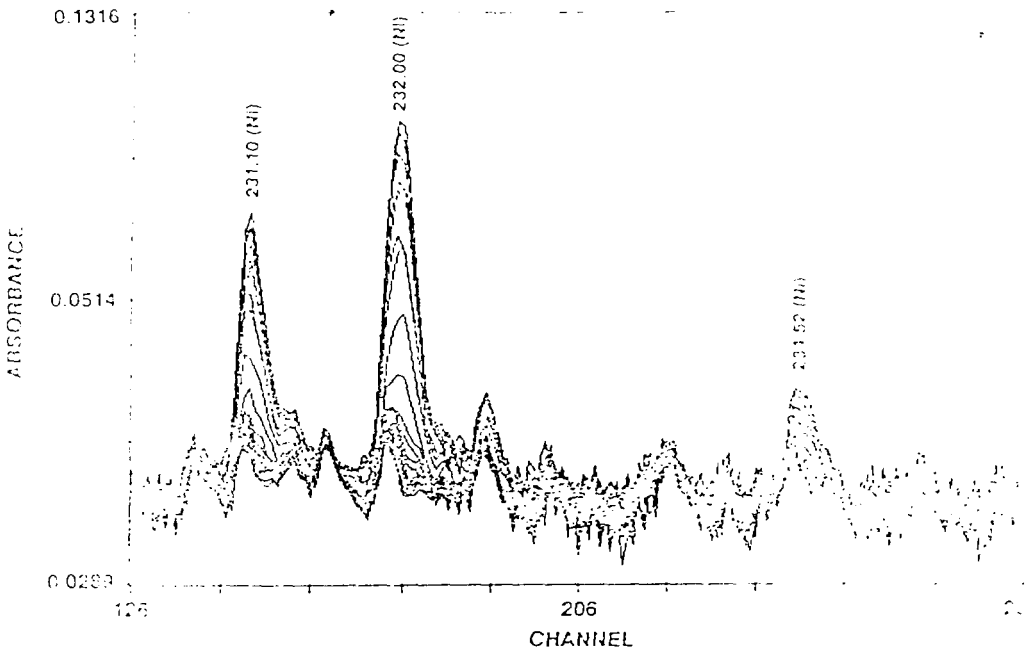


Figure 5a. Expanded time-resolved absorbance spectra of Ni-Co-Fe during atomisation in a graphite furnace : region of Ni absorption lines

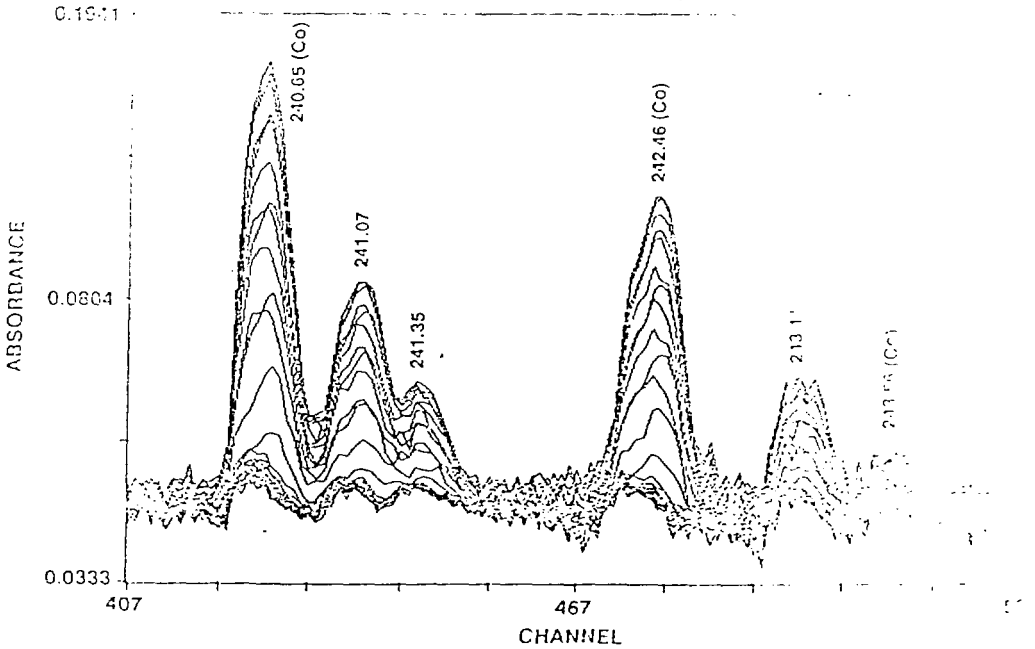


Figure 5b. Expanded time-resolved absorbance spectra of Ni-Co-Fe during atomisation in a graphite furnace : region of Co absorption lines.

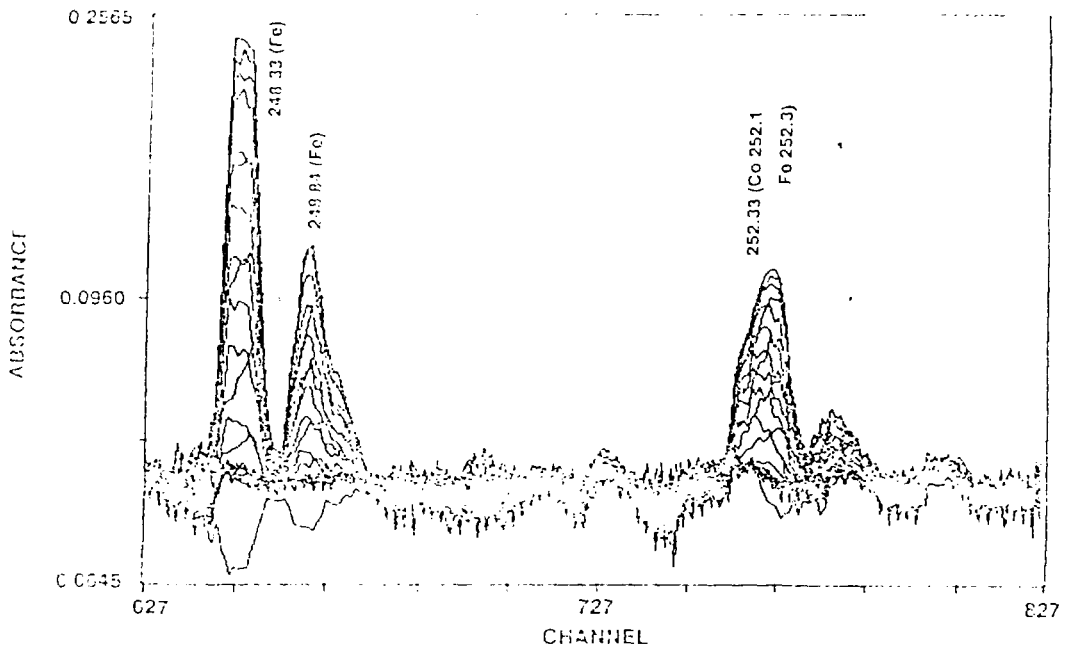


Figure 5c. Expanded time-resolved absorbance spectra of Ni-Co-Fe during atomisation in a graphite furnace : region of Fe absorption lines.

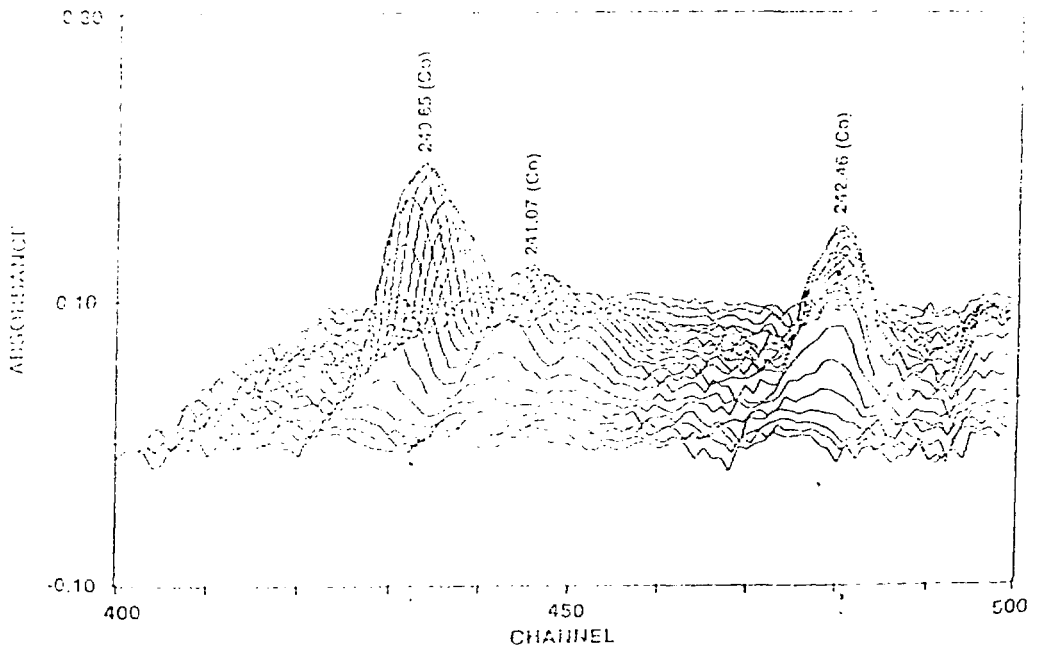


Figure 6. Expanded 3-dimensional time-resolved absorbance spectra of Co during atomisation in a graphite furnace.

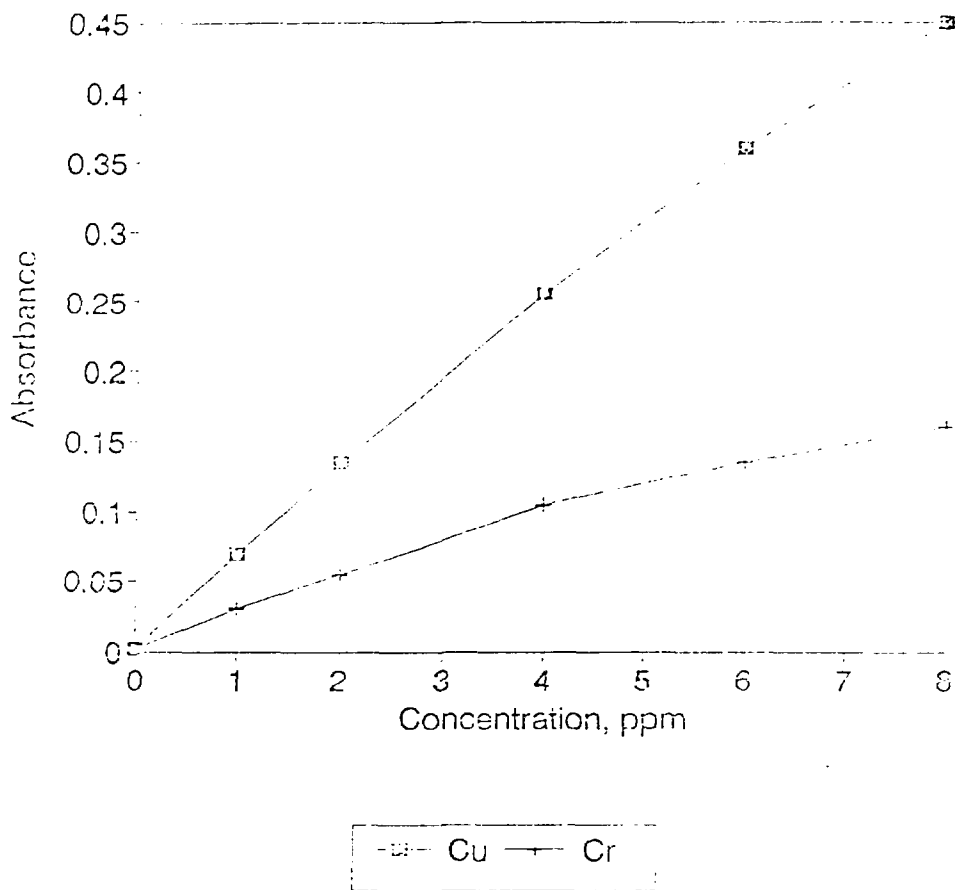


Figure 7. Calibration curves for Cu and Cr by simultaneous multi-element flame AAS using photodiode array detection.

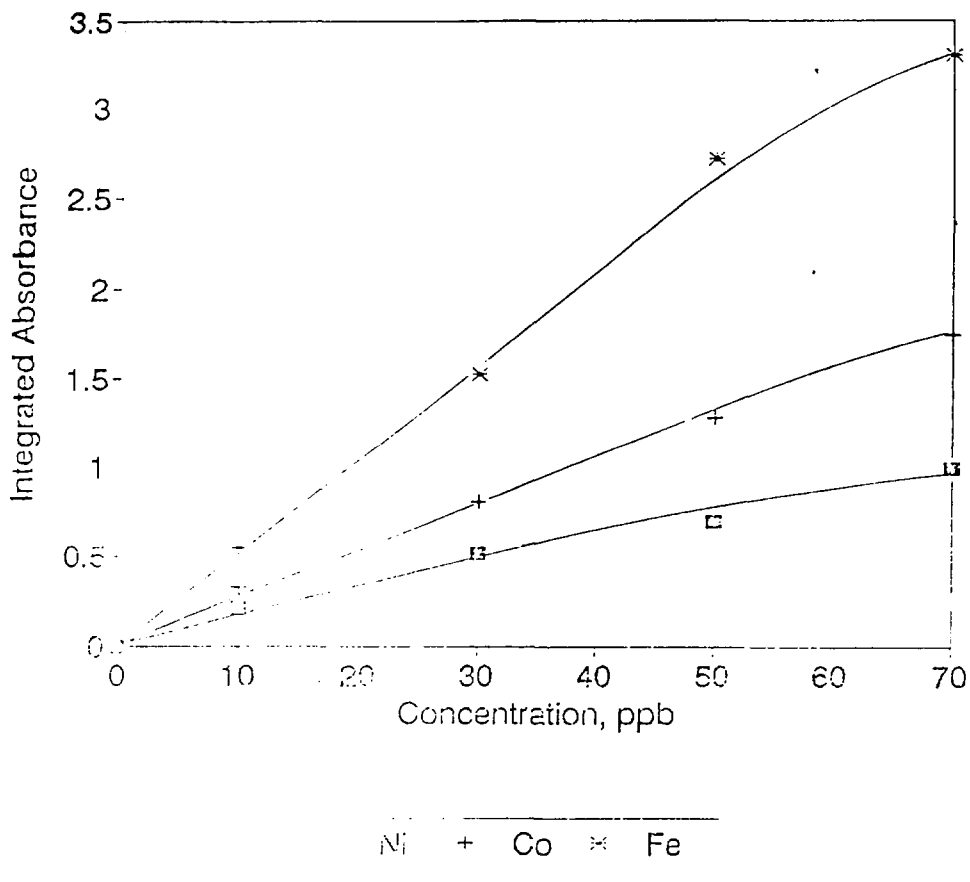


Figure 9. Calibration curves for Ni, Co and Fe by simultaneous multielement graphite furnace AAS using photodiode array detection.

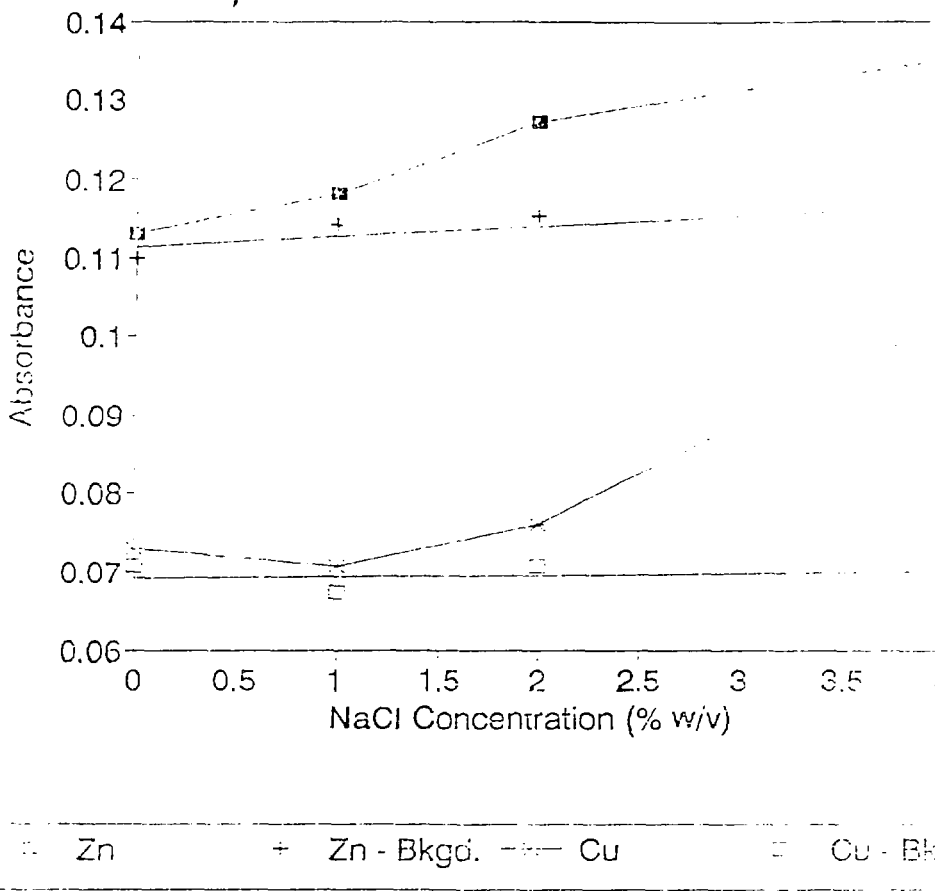


Figure 9. Absorbance of 1 ppm Cu and Zn solutions with and without non-atomic absorption corrections by simultaneous multielement flame AAS.

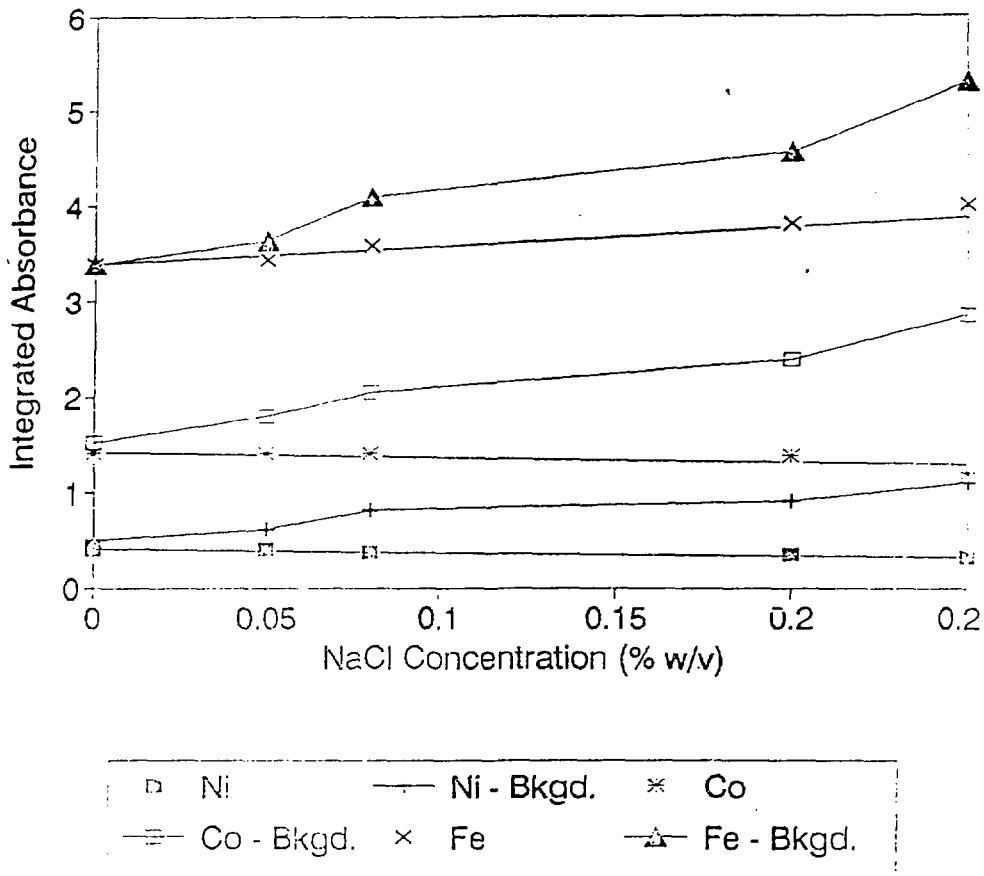


Figure 10. Absorbance of 70 ppb Ni-Co-Fe solutions with and without non-atomic absorption corrections by simultaneous graphite furnace AAS.