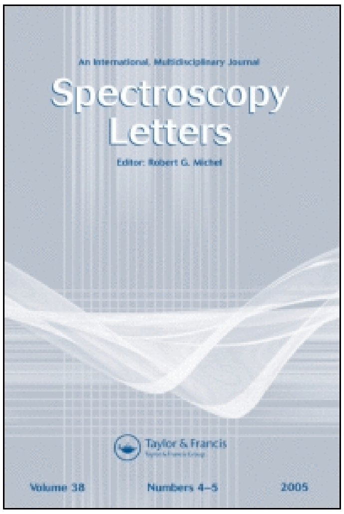

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Atomic Emission/Fluorescence Spectrometry with Second Derivative Wavelength Modulation and Its Application to Analysis of Copper Alloy

O. Kujirai[ab]; L. Davis[a]; J. D. Winefordner[a]
[a] Department of Chemistry, University of Florida, Gainesville, Florida [b] Material Properties Division, National Research Institute for Metals, Tokyo, JAPAN

To cite this Article Kujirai, O. , Davis, L. and Winefordner, J. D.(1985) 'Atomic Emission/Fluorescence Spectrometry with Second Derivative Wavelength Modulation and Its Application to Analysis of Copper Alloy', Spectroscopy Letters, 18: 10, 781 — 789

To link to this Article: DOI: 10.1080/00387018508062310

URL: http://dx.doi.org/10.1080/00387018508062310

SPECTROSCOPY LETTERS, 18(10), 781-789 (1985)

ATOMIC EMISSION/FLUORESCENCE SPECTROMETRY WITH SECOND DERIVATIVE WAVELENGTH MODULATION AND ITS APPLICATION TO ANALYSIS OF COPPER ALLOY[†]

Key Words: Atomic Emission/Fluorescence Spectrometry, Wavelength Modulation Sinusoidal Wave, Analysis of Copper Alloy

O. Kujirai[*], L. Davis and J.D. Winefordner[+]

Department of Chemistry, University of Florida,
Gainesville, Florida 32611

ABSTRACT

Atomic emission and fluorescence signals were collected simultaneously with sinusoidal wavelength modulation and detection of the second harmonic mode. The system consisted of a continuum source, argon-separated air/acetylene flame and a wavelength-modulated monochromator. Limits of detection of several elements were measured. This method was applied to the analysis of a copper alloy, and Co, Cu, Fe, Mn, Ni, Pb and Zn were successfully determined.

INTRODUCTION

With continuum source atomic fluorescence spectrometry (AFS), one light source can be used for the determination of many elements. Troublesome lamp alignment and time-consuming warm-up of individual lamps, otherwise necessary for each element, are avoided. Therefore, continuum source AFS is suitable

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[†] Research supported by AFOSR-F49620-84-C-0002.

[*] On leave from Material Properties Division, National Research Institute for Metals, Meguro-ku, Tokyo 153, JAPAN.

[+] Author to whom correspondence should be sent.

0038-7010/85/1810-0781$3.50/0

for sequential multielement determination, especially when the system is computer-controlled[1]. A Xe arc lamp, which has a high intensity over a relatively wide wavelength region, is generally used as the continuum light source. Signal modulation, to reduce background noise, is generally performed by mechanical chopping of the light source (amplitude modulation). Amplitude modulation, however, can not minimize noise sources related to flicker in the light source, such as scattering. Wavelength modulation, an alternative to amplitude modulation, is known to be effective in the minimization of low frequency flicker noise arising from molecular band absorption and emission and source scattering in atomic absorption and emission spectrometry[2,3]. Wavelength modulation involves rapidly scanning or stepping on and off the analytical wavelength. Wavelength modulation in AFS results in signals consisting of both emission and fluorescence[4]. In the previous study on continuum source atomic emission/fluorescence spectrometry (AE/AF), a stepped-square wave was used for wavelength modulation with second derivative detection[4]. The wavelength-modulated continuum source AE/AF was computer-controlled and showed flexibility for choice of wavelength and performance. This method was applied to the determination of trace elements in biological samples and jet engine lubricating oils[4].

In the present AE/AF study with continuum source excitation, a quartz refractor plate was sinusoidally modulated and second harmonic detection was used. Limits ot detection of several elements were measured and compared with those using other modulation methods. Second derivative AE/AF is suitable for the analysis of trace metals in metallic matrices, such as metals and alloys, because of the ability to minimize noise. The present system was applied to the analysis of trace metals in a copper alloy.

EXPERIMENTAL

Apparatus

The experimental set-up for the continuum source wavelength-modulated AE/AF system was similar to the one used in previous work[4], although the computer system, photon counter and mirror to reflect an additional image of the light source onto the flame were not used. A 300 W CERMAX Xenon arc lamp, operated at 15 V and 20 A, was used as the excitation source with an CERMAX model PS 300-1 power supply. The optical system consisted of a f4, 4-in focal length lens to focus radiation from the source onto the flame and a f5.3, 2-in focal length lens in a 2f configuration to focus a 1:1 image of the flame onto the entrance slit of the monochromator. A laboratory-made circular stainless steel capillary burner[5] and a Perkin-Elmer pneumatic nebulizer were used. A fuel-lean pre-mixed, argon separated, air/acetylene flame was used as an atomization cell (fluorescence) and atomization-excitation cell (emission). Argon was used as a sheath and separation gas around the flame. Flame conditions used were: nebulization air 6.5 l/min; auxiliary air 2.5 l/min; acetylene 1.3 l/min; and argon 7.5 l/min. The observation height was 19 mm above the burner top. The aspiration rate of the nebulizer was 7.4 ml/min. A GCA/McPherson model 218 monochromator, 0.3 m, f/5.3 Czerny-Turner with a 600 grooves/mm grating blazed at 300 nm, was used. The monochromator slit width and height were 75 μm and 10 mm, respectively. A Superior Electric model M063-FC06 C2 stepping motor was used for the sequential slew-scan. The resolution of each step was 0.5 Å. Wavelength modulation was carried out by inserting an oscillating Suprasil quartz refractor plate (0.125 x 1 x 1-in) just behind the entrance slit. The quartz refractor plate was attached to the connecting shaft of a General Scanning model G300 PDT torque motor which was controlled by a General Scanning model CCX101 scanner servo controller. The torque motor was driven by a sinusoidal wave from a Wavetek model 180 sweep/function generator. A Hamamatsu 1P28 or an EMI 9789 QB, powered by a Keithley model 244 power supply, was used as the photomultiplier tube. An a.c. signal from the photomultiplier tube was detected by a Keithley model 840 lock-in amplifier which was tuned to twice the frequency of the oscillating quartz plate. A 10 s integration time was used for all measurements.

Chemicals and Solutions

Nitric acid and hydrochloric acid were of analytical reagent grade. Water was deionized and further purified using a Barnstead Nanopure filtration system, and used throughout the experiment. High-purity metals were used for the preparation of stock standard solutions (1000 μg/ml). Cobalt, Cu, Mn, Ni and Pb were dissolved in dilute nitric acid. Iron and Zn were dissolved in dilute hydrochloric acid. Stock standard solutions were serially diluted with dilute acid. Tin was dissolved in concentrated hydrochloric acid and the solution was diluted to 6 M hydrochloric acid solution (stock standard solution). Ten V/V % hydrochloric acid solution was used to prepare dilute Sn solutions.

Analysis of Copper Alloy

NBS Standard Reference Material (SRM) 157A copper-nickel-zinc alloy was used for the experiment. The alloy sample was dissolved in a (3 + 1) mixture of nitric acid and hydrochloric acid. Synthetic standard solutions were matrix-matched to the sample solution with respect to elements and acids in order to prepare the analytical calibration curves. Concentrations of analytes were calculated by interpolating between standard solutions having lower and higher concentrations of analytes in the linear range of the log-log analytical growth curve.

The dissolution procedures used for the determination of Mn is typical of the analytical procedures used for all elements in the alloy. A 0.25 g of the alloy samples was weighed and moistened with water. A 2.5 ml of (3 + 1) mixture of nitric acid and hydrochloric acid was added. The solution was warmed to complete dissolution. After cooling. the solution was transferred to a 100-ml volumetric flask and diluted to the mark with water.

For the determination of the other elements, sampling weight, acid volume and dilution were adjusted appropriately in consideration of the linear dynamic range of the analytes in the analytical calibration curve.

RESULTS AND DISCUSSION

Optimization of Wavelength Modulation

To reduce spectral interferences, a 75 μm monochromator slit width (entrance and exit slits) was used. This is the same as used in the previous work[4]. The monochromator spectral bandpass of 0.6 nm was produced by using the defocused image due to the presence of the quartz plate in the optical path. The modulation frequency and deflection angle of the quartz plate were optimized for maximum signal using the Mn 279.5 nm line. The maximum signal was obtained at 110 Hz frequency of the sinusoidal wave and ±6.8 degrees deflection of the quartz plate. This frequency is much higher than the 12.5 Hz in the stepped-square wave case[4] and sufficiently rapid to reduce background flicker noise.

Limits of Detection (LODs)

In TABLE 1, LODs for seven elements measured by the AE/AF system are given. These elements were chosen because the copper alloy available contained these elements as major and minor elements. Flame conditions were adjusted by using a 100 μg/ml solution of Mn; therefore, they may not be optimal for the other elements but should be close. Wavelengths used were chosen to give the highest sensitivities and lowest LODs for emission plus fluorescence. The LOD was defined as the concentration giving a signal three times the standard deviation of sixteen measurements of the blank acid solution[6]. The LODs were compared in a fuel-lean and a slightly fuel-rich flames in TABLE 1. The LODs were nearly the same for both flame conditions. These results are not inconsistent with a previous noise study where the slightly fuel-rich flame generally has lower noise[7]. The difference between our results and those by Fujiwara, et al[7] is related to the use of sinusoidal modulation with second harmonic detection in the present study and the use of the d.c. detection system by the latter workers[7]. Source induced flicker noise is the main component of total noise[7].

TABLE 1

Limits of Detection Obtained for Seven Elements in Aqueous Solution (μg/ml)

		AE/AF (This Work)				
Element	Wavelength (nm)	Fuel-lean[a]	Slightly Fuel-rich[b]	AE/AF[c]	AE/AF[d]	AFS[e]
Zn	213.9	0.3	0.5	--	0.05	0.02
Co	240.7	1	1	--	0.1	0.02
Fe	248.3	2	2	--	0.08	0.02
Mn	279.5	0.1	0.07	--	0.006	0.004
Cu	324.8	0.08	0.07	0.3	0.01	0.007
Ni	352.5	0.2	0.2	--	0.08	--
Pb	405.8	2	1	1	0.2	0.2

[a] Sinusoidal Wave Modulation. Nebulization Air 6.5 l/min; Auxiliary Air 2.5 l/min; Acetylene 1.3 l/min; Ar 7.5 l/min.

[b] Sinusoidal Wave Modulation. Nebulization Air 6.5 l/min; Auxiliary Air 2.5 l/min; Acetylene 1.7 l/min; Ar 7.5 l/min.

[c] Values Taken from Reference 8. Without Modulation. Argon-separated Air/Acetylene. LODs Defined as Twice Standard Deviation above Background.

[d] Values Taken from Reference 4. Stepped-square Wave Modulation. Nitrogen-separated Air/Acetylene.

[e] Values Taken from Reference 4. Amplitude Modulation. Nitrogen-separated Air/Acetylene.

For comparison purposes, TABLE 1 includes the LODs for cases of no modulation[8], amplitude modulation[4] and wavelength modulation where the second harmonic detection mode of a stepped-square wave was used[4]. From TABLE 1, the LODs in the sinusoidal wave modulation case were similar to those in the unmodulated continuum source AE/AF case[8]. In the latter case, flicker noise due to source scatter, source induced background fluorescence and flame emission were more serious than in our case. The LODs for our sinusoidal wave modulation case were about 35X worse than those for the amplitude modulation[4] (average of six elements) case and an order of magnitude worse than those using stepped-square wave wavelength modulation[4] (average of seven elements). In this study, all measured wavelengths were under $\approx$350 nm except for Pb;

elements whose transitions are below ≈350 nm consist primarily of fluorescence[4]. Poorer LODs for these elements in the wavelength modulation case in Reference 4 were explained as a result of the loss in signal by the presence of the quartz plate within the monochromator. Most likely, the LODs are poorer in our sinusoidal wave modulation case than in the previous stepped-square wave modulation system[4] because of the less efficient waveform used and the lack of a photon counter and a source mirror. In our sinusoidal wave modulation system, the average light flux reaching detector was significantly less than with stepped-square wave modulation[9]. This resulted in a signal loss. With the second harmonic detection mode in atomic emission spectrometry[9], the loss in flux was about a factor of four in going from stepped-square wave to sinusoidal wave modulation. By means of computer modeling of the second harmonic mode of wavelength modulation[10], square wave modulation offered a signal-to-noise ratio advantage of approximately a factor of two compared with the sinusoidal wave modulation for a shot noise limited system.

Therefore, the linear dynamic range of the analytical growth curve was relatively small with second harmonic mode sinusoidal wavelength modulation. The linear dynamic range was about an order of magnitude for Co and Zn, and two orders of magnitude for Cu, Fe, Mn, Ni and Pb.

A fuel-lean flame was used for the analysis of the copper alloy by considering the LOD of Zn and the lower scattering by copper salts (20 mg/ml) in the fuel-lean air/acetylene flame[11]. Lower scattering is preferred for the analysis of copper alloy with a high matrix concentration even when wavelength modulation is used. The amount of band structure or the continuum background which can be tolerated with the wavelength modulation will depend on the optical system and the photodetector[3].

Analysis of Copper Alloy

Two factors should be considered for the analysis of real samples: spectral interferences; and nebulization efficiency. The former factor is critical for the determination of minor or trace elements in the presence of

TABLE 2

Analytical Results of NBS SRM 157A Copper-Nickel-Zinc Alloy

Element	Certified Value (%)[a]	Found (%)[b]
Zn	29.09	30.0
Co	0.022	0.022
Fe	0.174	0.167
Mn	0.174	0.178
Cu	58.61	59.3
Ni	11.82	11.8
Pb	0.034	0.029

[a] SRM 157A also Contains 0.021 % of Sn and 0.009 % of P.

[b] Average of Two Measurements.

high matrix concentration using a low or medium resolution monochromator. The latter factor introduces errors when the sample solution with high matrix concentration is analyzed with standard solutions containing only analyte. The matrix-matched calibration curve method was used to compensate for these effects.

Analytical results of the copper alloy are shown in TABLE 2. The results agree well with the certified values from the main components to minor components in the copper alloy, and from the dilute solutions to concentrated solutions. Several dilutions of the sample solution were prepared in order to obtain analyte concentrations within the linear dynamic ranges.

The measurement of Sn in NBS SRM 157A was attempted. The 303.4 nm line and a relatively fuel-rich flame were used to avoid interferences[12] (nebulization air 6.5 l/min; auxiliary air 2.5 l/min; acetylene 2.0 l/min; and Ar 7.5 l/min). Under these conditions, the LOD of Sn was 5 μg/ml and the upper limit of the linear dynamic range was 200 μg/ml. The copper alloy sample was dissolved in the (3 + 1) mixture of nitric and hydrochloric acids. The solution was dried and the residue was dissolved in 0.15 M hydrochloric acid solution to prevent the precipitation of Sn as the oxychloride. For some reason, the analyte signal and blank gradually increased with measurement time preventing the determination of Sn.

Although wavelength modulation using second harmonic mode detection has fairly high LODs and fairly small linear dynamic ranges, it minimizes background noise and is suitable for the analysis of real samples. Lower LODs and larger linear dynamic ranges will be obtained by changing the excitation source from a Xe arc lamp to a dye laser or an ICP and/or atomization and excitation cell to an ICP although the excellent characteristics of the continuum source AE/AF are lost.

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Received: 06/14/85
Accepted: 07/16/85