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FEASIBILITY OF USING A URANIUM HOLLOW CATHODE LAMP AS PRIMARY SOURCE IN ATOMIC ABSORPTION SPECTROSCOPY

by

G. ROSSI and N. OMENETTO

1967

Joint Nuclear Research Center
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SUMMARY

The feasibility of a Uranium hollow cathode lamp, working at high discharge current, as primary source in atomic absorption spectroscopy is presented.

The extreme complexity of the Uranium spectrum makes possible the coincidence of its lines with the analytical resonance lines of the most of the elements. Uranium is excited in a Ni hollow cathode at 500 mA discharge current. The advantages to have at a disposal this multi-line source are stressed. First results are then presented for the elements Cu, Mg, Mn, Fe, Ni, Cr and In.

FEASIBILITY OF USING A URANIUM HOLLOW CATHODE LAMP AS PRIMARY SOURCE IN ATOMIC ABSORPTION SPECTROSCOPY(+)

INTRODUCTION

Among the different instrumental parameters involved in atomic absorption analysis, the emission source together with the means of sample atomisation, were the most widely investigated (1,2,3,4,5,6,7,8,9).

The use of the popular hollow cathode lamps is mainly limited by a noticeable investement in a multiplicity of lamps required for the analysis of the various elements and by the unfavorable ratio between the time required for interchanging the sources and warming-up ($\sim$25 minutes) and the effective time of measurement ($\sim$30 seconds). Multi-element hollow cathode lamps - lamps with cathodes containing up to 6 elements now commercially available - offer partial solutions to this problem. On the other hand, the use of demountable lamps (3,4,5,6) in which cathodes can be rapidly replaced, represents a more economical approach to the problem, but the inconvenience connected to the time loss still exists. Moreover, difficulties in the preparation of cathodes for some of the elements, must be taken into account. Walsh's conclusions (7) on the feasibility of using a continuum as primary source showed that a high resolution monochromator would be required in order to isolate the spectral profile of the absorption line (0,01 - 0,03 A°) and that low energy would be available in that narrow frequency interval.

However, Fassel et al (8) and subsequently W. McGee and J.D. Winefordner (9) have demonstrated that a continuum of high stability connected with a medium resolution monochromator can give results either comparable to or exceeding those obtained with sharp-line sources. As reported by L. De Galan et al (10) only at low atomic concentration does a linear relationship exists between either absorbance or absorption values versus concentration. However, the high stability of the continuum source allows for an appropriate scale expansion to be used in order to measure the low absorption values.

Sharp-line sources are still superior as far as it concerns the slope and the concentration range of the working curves.

(+) Manuscript received on May 20, 1967.

Obviously, the "ideal source" for atomic absorption would be such a lamp whose spectrum includes all the analytical lines of the elements. A good approach to this source, practically unrealizable, would be represented by a lamp containing an element which emits as many lines to make of analytical use the coincidences with the resonance lines of the other elements. In this sense, C.W. Frank et al (11) have reported analytical results for Mg, Mn, Ni and Cu, by using as primary source a Westinghouse Iron hollow cathode lamp. In this connection, some other factors must be taken into account: the frequency difference between the absorption lines in the flame and the emission lines, the energy of the latter, and the instability of this source, greater than that of the continuum, which limits the usefulness of the scale expansion when unfavorable signal to noise ratios are concerned.

These factors suggested to us the opportunity to consider a Uranium hollow cathode lamp as a possible primary source. As well known, the Uranium spectrum is by far the most complicated among the spectra of all natural elements. D.W. Steinhaus (12) estimated 30 lines per Angstrom as a mean value for the Uranium spectrum. In other words, the spectrum will appear like a continuum with a medium resolution monochromator. In these conditions, a very large number of coincidences between U lines and analytical lines of the other elements should exist. Table I shows the resonance wavelengths for a large number of elements and the corresponding wavelengths of Uranium lines, taken from M.I.T Wavelengths Tables (13). The extreme complexity of the Uranium spectrum is not accompanied by a corresponding remarkable emission intensity. However, previous works (14,15) on Uranium isotopic analysis, showed that a rather high spectral intensity was obtained by exciting Uranium in a water-cooled hollow cathode lamp operated at high current rate (500 mA) and in the presence of Argon. Uranium, in the form of U_3O_8, was deposited in a Ni cathode with 3 drops of concentrated HF, followed by drying. The use of a Uranium metal diso

in the cathode led to a more stable discharge together with a much higher emission intensity and a longer life-time of the lamp. For each particular wavelength, a discharge current rate and an entrance slit width can be choosen in order to bring the output energy to a level of analytical value. However, a good coincidence will not always mean that an absorption will take place. Some factors like the intensity, the spectral band width and the possibility of self-reversal of the emission line can make the coincidence ineffective for the absorption. For these reasons Frank et al. (11) were not able to achieve the expected results for the Mg whose line is exactly coincident with an Iron line at 2852,13.

PRELIMINARY RESULTS AND DISCUSSION

This report describes the preliminary results obtained by using a Uranium hollow cathode lamp as emission source. Fig. 1 shows a block diagram of the apparatus. Incident radiation from the Uranium lamp is reflected by a plane mirror in the optical path of an atomic absorption spectrometer. This arrangement allows for a fast conversion of the apparatus to operate with conventional hollow cathode tubes by simple tilting of the mirror.

Table II summarizes the specific components of the experimental set-up and the operating conditions. Table III lists a first series of elements and the results obtained. It must be pointed out that the experimental conditions were in no case optimized because the aim of this work was to demonstrate the feasibility of using the Uranium hollow cathode lamp as primary source rather than a critical evaluation in terms of sensitivity.

Nevertheless the sensitivites for the elements Cu, Mg and Mn are comparable to those obtained in the same conditions with their sharp-line sources.

CONCLUSIONS

The results obtained look undoubtly promising and seem to confirm the broad analytical applicableness of a very complex line source in atomic absorption. Noticeable improvements should be expected by the use of a more sophisticated detection and recording system as well as that of a nitrous-oxyde acetylene flame for the refractory materials.
Tests for other elements and a critical evaluation of the different parameters (lamp current, spectral band width of the monochromator and flame conditions) are now in progress. The results will be presented in a future paper.

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TABLE I

Analytical lines of the elements with the corresponding Uranium lines which should show absorption.

Element	λ(A°)	U λ (A°)	U int. arc.	U int. spark.
Ag	3280.683	3280.608	1	2
	3382.89	3382.67	4	4
Al	3092.71	3093.012	20	20
Au	2427.95	2427.622	12	2
B	2497.733	2498.267	3	8
Ba	5535.551	5535.796	6	2
Be	2348.61	2348.91	2	2
Bi	3067.716	3067.758	8	6
Ca	4226.728	4226.60	1	2
Cd	2288.018	2287.80	-	2
Ce	2761.415	2761.449	5	2
Co	2407.254	2406.435	10	10
Cr	3578.69	3578.327	8	1
Cu	3247.54	3247.709	4	5
Dy	4211.719	4211.68	10	10
Er	4007.67	4007.934	8	3
Eu	4594.02	4594.294	6	8
Fe	2483.27	2484.008	15	4
	3719.94	3719.69	1	8
Ga	2874.244	2874.083	15	10
Gd	3684.124	3684.617	5	5
Ge	2651.575	2651.844	3	15 h
Hf	3072.877	3072.783	20	20
Hg	2536.519	2536.6	3	2
Ho	4053.92	4054.313	12	15
Y	4102.376	4102.21	1	4
Yb	3987.994	3988.029	8	12
In	3039.356	3039.263	15	12
	2502.983	2502.407	2	10

Element	λ(A°)	Uλ(A°)	U int. arc.	U int. spark.
La	3574.426	3574.11	12	8
Lu	3081.47	3081.66	6	4
Mg	2852.129	2852.469	6	4
Mn	2794.817	2795.235	18	12
Mo	3132.594	3131.987	8	6
Nb	3580.273	3580.244	6	1
Ni	3414.765	3413.806	4	10
Os	2909.061	2909.25	6	15
Pb	2833.069	2833.244	8	4
Pd	2476.418	2476.474	2	8 h
Pt	2659.454	2659.025	8	2
Re	3460.47	3460.351	3	5
Rh	3434.893	3435.20	10	-
Ru	3498.942	3499.071	6	8
Sb	2311.469	2310.67	-	10
Sc	3907.476	3907.558	6	8
Si	2516.123	2515.729	6	2
Sm	4296.75	4297.11	18	18
Sn	2863.327	2863.44	6	4
Ta	2714.674	2714.584	10	8
Tb	4318.85	4319.056	1	5
Tl	2767.87	2767.413	5	4
Tm	4094.18	4093.994	12	3 h
V	3183.406	3182.833	6	8

TABLE II

Specific components of the apparatus and operating conditions

Emission source	Water-cooled Uranium hollow cathode Lamp-Ni cathode with a 10 mm outer diameter and with a 6 mm diameter, 15 mm deep cavity. Uranium metal disk 3 mm thick, 6 mm diameter pressed on the bottom of the cathode. The lamp was operated by a RSV stabilized d.c. power supply, delivering up to 500 mA discharge current by steps. The flowing gas was Ar at a pressure of 1 Torr.
Optics	Five pass system
Monochromator	Jarrell-Ash 0,5 m Ebert grating monochromator equipped with a 1250 lines/mm grating blazed at 3000 A° and variable slits
Detector and associated electronics	RCA 1p28 photomultiplier (2000 - 5000 A°) Regulated Jarrell-Ash d.c. power supply. The d.c. photomultiplier output signal was fed into a Keithley micromicroammeter mod. 414 and displayed on a 10 mV Dynamaster strip-chart Bristol recorder.
Flame	Air-Hydrogen flame at a pressure of 20 psi and 1,16 psi respectively
Burner	Total consumption Ditric corporation HETCO burner.

TABLE III

Sensitivity and operating conditions

Element	Analytical line (A°)	Uranium line (A°)	Slit width (μ)	Lamp current (mA)	Sensitivity +)
Fe	3719.94	3719.69	20	500	4
Ni	3414.77	3413.806	10	500	5
Cr	3578.69	3578.327	30	500	5
Mn	2794.817	2795.232	10	500	0,5
Mg	2852.13	2852.469	50	250	0,05
Cu	3247.54	3247.709	10	500	0,5
In	3039.356	3039.263	10	500	10

+) Values are referred to that concentration which produces a 2% absorption

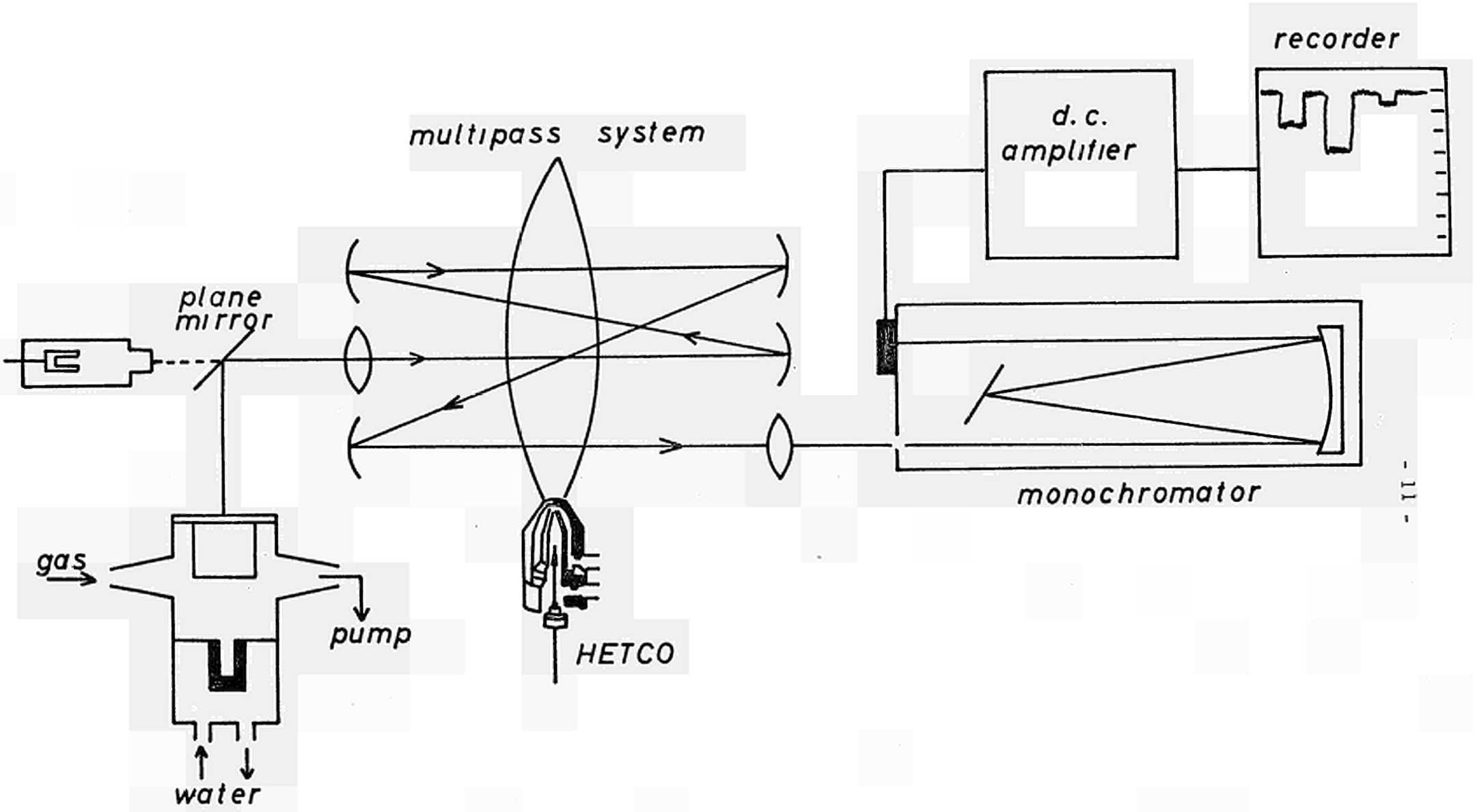
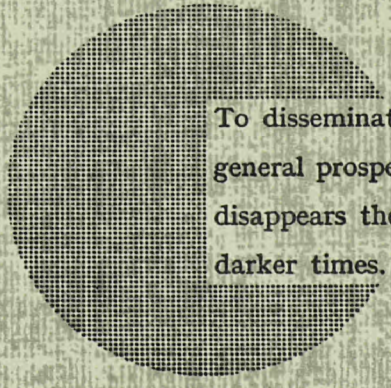


Fig 1 Block diagram of the apparatus



To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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