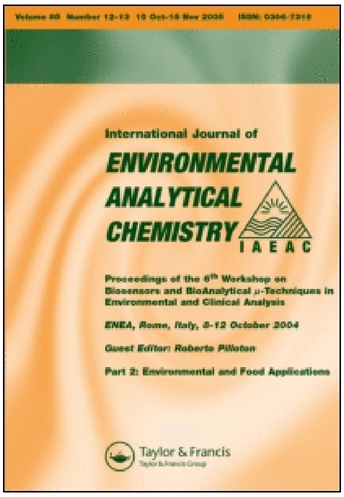

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A NEW COMBINED ELECTROTHERMAL HOLLOW CATHODE ATOM AND EMISSION SOURCE, AND ITS APPLICATION FOR WATER ANALYSIS

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A new radiation source based on the FANES-method has been developed in order to achieve an intensity enhancement of the radiation produced. Investigations carried out on our new source are controlled by a computer system connected with a multichannel spectrometer having a wavelength modulated background corrector. Beside description of the system, the results of analysis of some water samples are also presented.

Keywords: Combined electrothermal hollow cathode source; simultenous multielement analysis; water analysis

INTRODUCTION

Several new combined atom and emission sources have been developed in the past one-two decades. Among others, these include the following combinations: laser-spark plasma, arc-spark aerosol generators for ICP, furnace-in-flame, etc. The so-called FANES-technique, Furnace Atomisation Non-Thermal Excitation Spectrometry [1-4] developed by Falk et al. [2] is the newest, combined simultaneous atom and multielement spectroscopic source. This source combines the advantages of micro-sampling and the capability of excitation of elements having high excitation energies. Nevertheless the radiation source described above has technical disadvantages, which have been eliminated in the radiation source described herein. In our previous papers, the development of electrothermal

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atomizers and radiation sources [5], as well as hollow cathode sources [6,7] are discussed. In the latest work, a sample holder electrode, forming an electrothermal vaporizer, was built axially into the cavity of a hollow cathode. The vaporizer and atomizer current or potential can be varied almost independently of the current and potential of the cavity. In Falk's method, the particles sputtered by the discharge into the graphite tube leave the tube during heating in equal ratios in both directions, marked x and x' Figure 1. part a). Thus, in the FANES method, only a maximum of 50% of the particles introduced into the graphite tube can reach volume "E", where most of the excitation and emission takes place. In our source (Figure 1. part b.), the graphite cup has a closed end opposite the anode, so the analyte introduced into the cup can leave it only towards the anode. In this way, in principle, 100% of the analyte gets into the volume "E", resulting in optimum excitation. According to the equation by Nowosielow-Zanmienski [8],

$$I \times d = \text{constant}.$$

It means, that the product of the radiation intensity, I, formed in the cavity of the hollow cathode source, and the diameter, d, of the cavity is constant. Consequently, in principle, if the diameter of the cavity is decreased, the intensity of the emitted light is increased, provided that other conditions remain unchanged.

Taking into account that the diameter of our graphite cup is only 2-3 mm, thus being 2 to 3 times smaller than that of FALK's tube (Figure 1), an increase of intensity of similar magnitude can be expected.

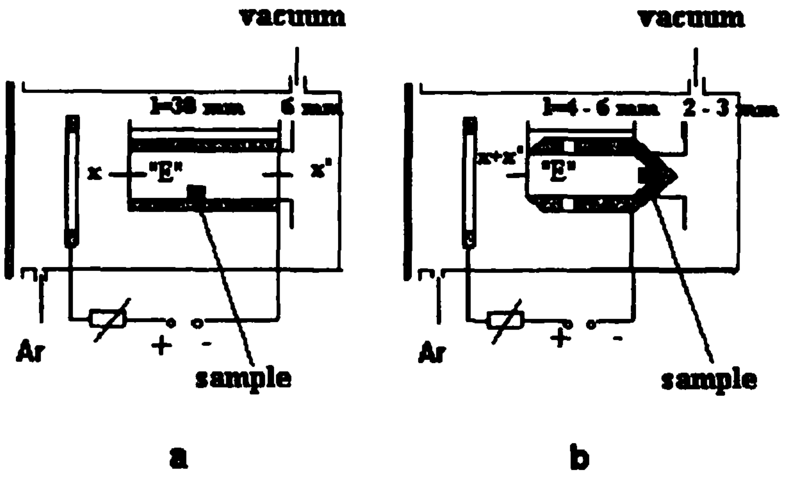

FIGURE 1 Comparison of the FANES device (a) to the source developed here (b)

EXPERIMENTAL CONDITIONS

Our system consists of the new radiation source, a programmable a.c.-d.c. power supply, a spectrometer, and a computer with a control program.

The Radiation Source

A schematic diagram of the developed source is presented in Figure 2. In this radiation source, 5-40 µl of the solution to be analysed is taken into the pyrolised graphite cavity by means of a micropipette. The solution can be introduced in the following way: the whole cathode holder part together with the cathode is pulled out and put back after the introduction of the sample (in this way a new cathode cup can also be replaced).

The Programmable Power Supply

The drying, thermal decomposition, vaporisation and atomisation are carried out by the a.c. part of the power supply. It is similar to conventional electrothermal atomizers. Both voltage controlled and temperature controlled heating method can be chosen. The first method is used during the thermal decomposition, while the later must be applied for the evaporation and atomisation. For thermal decomposition performed on higher temperature, (e.g. 800-1100 °C) temperature controlled heating method can be choosen either. The sample is excited by a 200-600 V current-modulated d.c. discharge between the anode and the cathode cup, under 100-600 Pa pressure of argon gas. The modulation is square-wave

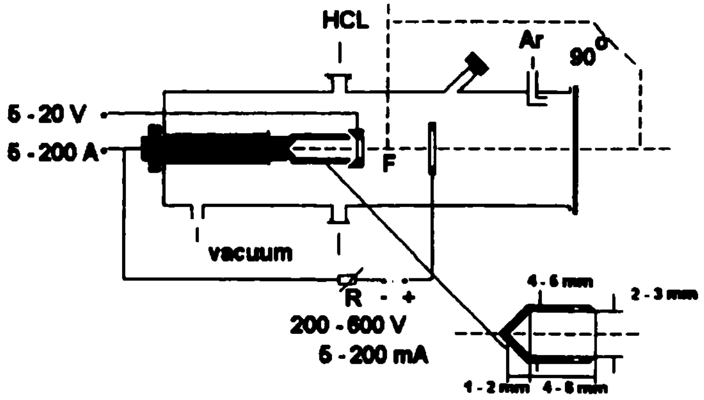

FIGURE 2 Schematic diagram of the present source

modulation, the low current is always 2.5 mA, while the value of the high current can be selected in the range of 15-50 mA. The power supply has a special interface, which is connected to the printer port of the computer. Both cup heating and modulation of the discharge are controlled by the computer.

The Spectrometer

The spectrometer used in our experiments has a concave gratings (Rowland mounting with a focal length of 2 meters, 1200 grooves/mm). Photomultiplier tubes are used as detectors. Its wavelength range is 200-800 nm. The entrance slit can adjusted between 20 and 200 μm. The optical system can accomodate 32 photomultiplier tubes, and it is equipped with a wavelength modulated background corrector using a vibrating quartz plate. The original measuring system of the spectrometer is not capable to process rapid signals, therefore the signals from the measured channels were led via a ribbon cable directly to a PCL 711 PC Multilab Card, (from the firm Advantech. Co. Ltd.) placed into an IBM compatible computer. This card performs the AD conversion of the measured signals, and does the background corrector control.

The Computer and the Control Program

An IBM compatible 286 AT computer is used to perform all the task necessary for the system control. It is supplemented with the above-mentioned PCL-711 card, for the background corrector control and A/D conversion of the signals coming from the spectrometer. The A/D converter of the PCL-711 card can handle eight analogue channels, so eigth lines can be measured simultaneously. The number of elements measured simultaneously can be increased by adding another PCL-711 card to the system. The 286 AT can accomodate it. In this way 16 elements can be measured simultaneously. A control program, written in Turbo Pascal of the Borland Inc., was developed for controlling the system. It ensures the possibility of developing heating programs (time, temperature values for the ashing and evaporation phase, and the feedback-mode, – voltage or temperature control, – can be selected). Furthermore, it controls the power supply and the background corrector, switches up and down the discharge current, reads out the channels of the A/D converter, and stores the measured data on hard disc. It is able to calculate the emission intensity and to perform the graphical presentation of the data. The beginning and the end of the signal-integration time can be selected within the whole measured time-period separately for each channel. From the timing diagram (Figure 3), it can be seen, that a 60 ms time is necessary

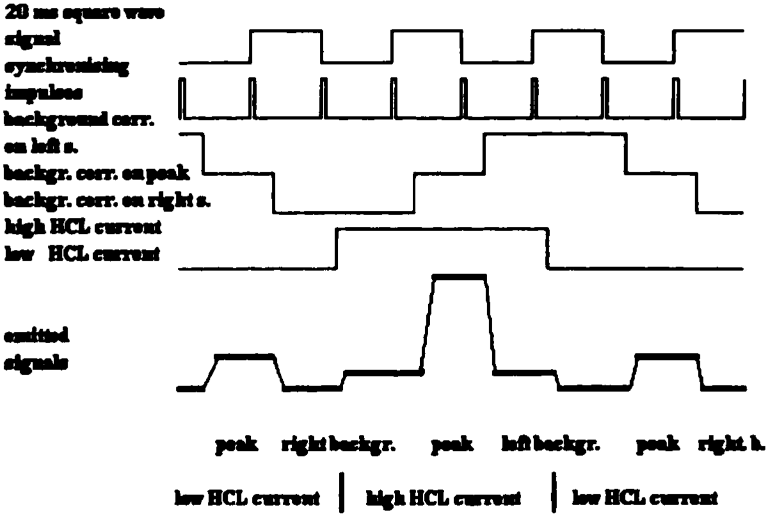

FIGURE 3 Timing diagram

to get a netto intensity value. The control sequence can be seen in Figure 4. The A/D conversions and their readout take place during the first 1 ms period. Then positioning of the background corrector must be started. After that, the discharge current must be changed (switched up or down). A 60 ms period seems too long for measuring of the rapid evaporation peak signals, therefore we developed another control method, in which the background corrector always is in its mid-

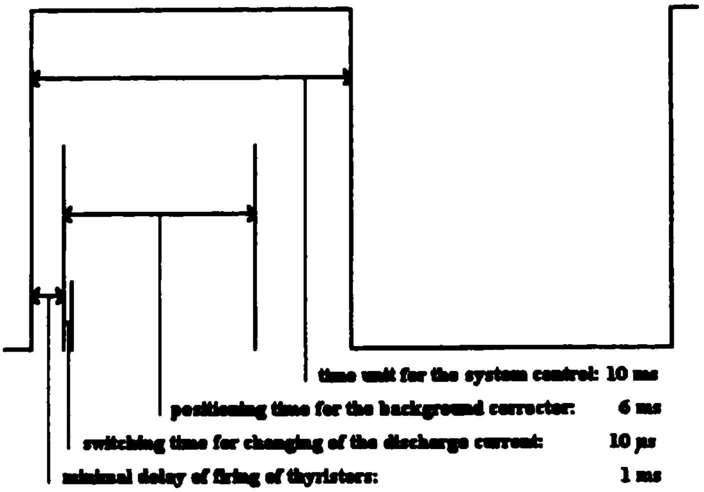

FIGURE 4 Control sequence within a control cycle

dle (on peak) position. As only the d.c. discharge has to be controlled in that case, therefore 20, or 10 ms time is necessary to get an intensity value. This method can only be applied when the background is low during the evaporation peak of the analyte, as there is no spectral background correction. The timing diagram of this simplified method can be seen in Figure 5.

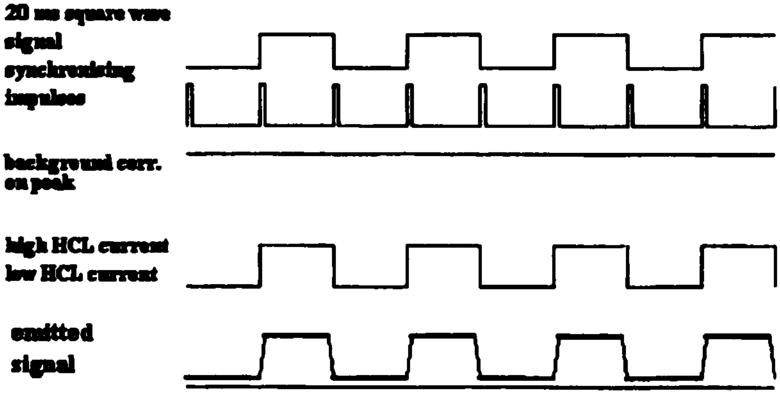

FIGURE 5 Timing diagram of the simplified control method

Other Permament Conditions

In order to get a stable discharge, the discharge current was switched periodically up to a high value, and down to a low value. The low current was always 2.5 mA. The high value was 35 mA. The heating program consists of a drying, two ashing, an evaporation and a cleaning phase. As water and dilute aqueous solutions boil at room temperature at a pressure of 2200-2300 Pa, the drying takes place at room temperature, the argon pressure is simply adjusted to a pressure of 2500-2600 Pa. In this case a sample of a 10 μl volume becomes dry in three minutes. In order to get the best optical performance, the wavelength values for the elements being measured must be selected from the most favourable spectral range of the spectrometer. In case of our spectrometer this was the range above 270 nm. On the other hand it must be taken into account that the longer is the wavelength selected for an element, the greater is the intensity of the thermal emission coming from the cup. As it will be shown, thermal emission can be encountered even at the beginning of the visible range. Therefore the measured lines were selected from the range of 270-450 nm. In the experiments the number of elements being measured simultaneously was 5, but it can be increased up to 16 in the above-written way. All the conditions are listed in Table I.

TABLE I Operating conditions

Measured elements and wavelength values:					
	Mn	Cu	Ni	Cr	Pb
λ[nm]	279.482	324.750	341.477	357.868	405.782
Entrance slit of the spectrometer: 60 μm.					
Sample volume: 10 μl					
Heating program:					
Drying:			room temperature/p(Ar) = 2500-2600 Pa/, 180 s		
Ashing I:			400 °C, 10 s		
Ashing II:			600 °C, 5 s		
Evaporation:			1800 °C, 10 s		
Cup cleaning:			2000 °C, 2 s		
Measured phase: ashing II and evaporation					
Discharge parameters:					
p(Ar): 266 Pa/except for the drying phase, see in the text/					
discharge control: square-wave method					
periodic time: 10 or 20 ms					
value of the low current: 2.5 mA					
value of the high current: 35.0 mA					
Measuring method: peak profile integration					

RESULTS

Thermal Emission

As the wavelength of the lines chosen are at the beginning of the visible region, or not far from it, the effect of thermal emission of graphite parts can be encountered in the course of the evaporation. The thermal emission of the empty graphite cup on different lines is presented in Figure 6. It can be seen, that the effect is negligible, except for lead. In Figure 7 the signal profile of an empty cup and a cup with 10 μl 1 μg/cm^{3}lead solution can be seen on the 405.782 nm Pb line. (The profile of the solution data is shifted upwards with 200 units.) From Figure 7 it is obvious, that the analytical peak of lead appears well before the thermal emission begins, so the effect of the thermal emission can be eliminated by the means of preselected signal-integration time values.

Detection Limits

In order to see if the system is really suitable for multielement determinations we determined the detection limits for five elements (Mn,Cu,Ni,Cr,Pb) from multi-

FIGURE 6 Thermal emission of the empty graphite cup on different wavelengths at 2000 °C

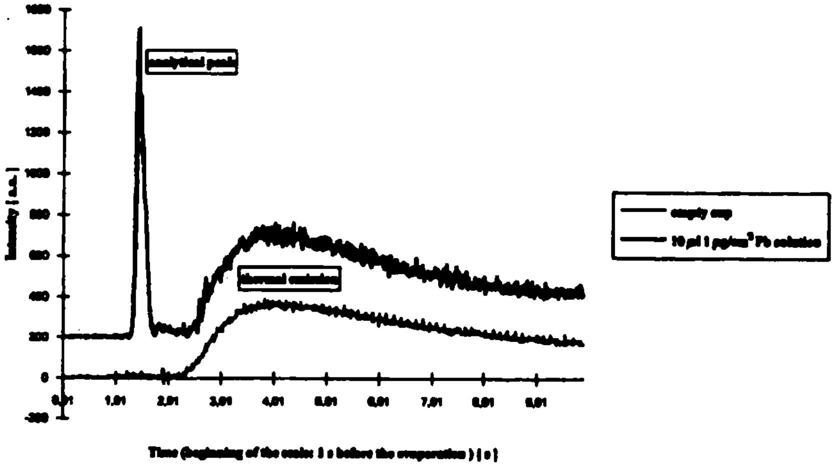

FIGURE 7 Full signal profile of the empty cup, and cup with 10 µl 1 µg/cm^3 Pb solution on 405.782 nm

element aqueous solution under the conditions listed in Table I. The solution contained all these five elements in a concentration of 0.2 µg/cm^3. The results calculated according to the 3σ criteria, are in Table II. The linearity was tested only in the range of 0.1-0.5 µg/cm^3, and it was found to be good, the correlation coefficients for the linearity, lay in the range of 0.990-0.996.

TABLE II Detection limits for five elements from multielement solution

Element	*Mn*	*Cu*	*Ni*	*Cr*	*Pb*
λ [nm]	279.482	324.750	341.477	357.868	405.782
RSD_{blank}[%]	6.5	1.7	1.8	1.9	3.2
DL[$\mu g/cm^3$]	0.0380	0.0014	0.0086	0.0084	0.0033
DL_{abs}[g]	3.8×10^{-10}	1.4×10^{-11}	8.6×10^{-11}	8.4×10^{-11}	3.3×10^{-11}

RSD_{blank}: relative standard deviation of the blank solution
DL: detection limit
DL_{abs}: absolute detection limit

Analysis of Water Samples

The reason for choosing water samples as real analytical samples, is the relatively little number of possible matrix effects existing in water. This choice also makes possible to apply the simplified control method. During preminilary experiments we made sure that no spectral interferences could be encountered on the selected wavelengths. Water samples were filtered and acidified with nitric acid to a concentration of 0.6 mol/dm^3. For calibration multielement aqueous solutions (containing all the five elements in a concentration range of 0.1-0.5 $\mu g/cm^3$) were used. In Figure 8 Mn and Pb peaks can be seen in a sample taken from the brook Boldva. In Figure 9

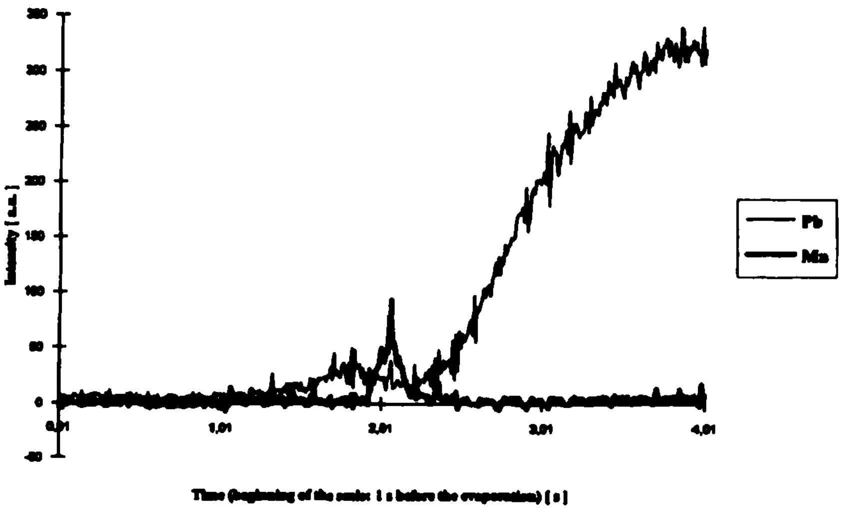

FIGURE 8 Pb and Mn peaks in a sample taken from brook Boldva

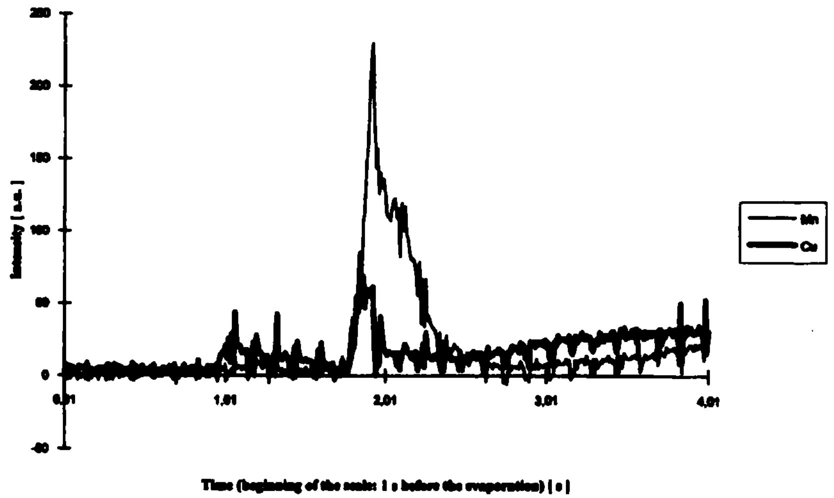

FIGURE 9 Mn and Cu peaks in a ground water sample

Mn and Cu peaks are presented from a ground water sample. The analytical results of some sample (compared to the values determined by an ICP-AES instrument, equipped with an ultrasonic nebulizer) are in Table III.

TABLE III Comparison of results of some water samples determined by the modified source and by ICP-AES instrument (ARL 3410), fined with ultrasonic nebulizer (all concentration in μg/cm^3)

Sample Element	*river Sajó*	*brook Boldva*	*ground water*	*tap water*
Mn	0.048	0.047	0.67	nd.
Mn (ICP)	0.063	0.041	0.64	0.017
Cu	0.005	nd.	0.009	0.0041
Cu (ICP)	0.0043	0.0007	0.010	0.0037
Pb	0.0052	0.0073	nd.	0.0049
Pb (ICP)	0.0047	0.0068	0.0020	0.0041

nd. : not detected (below the present detection limit value)

CONCLUSIONS

Comparing the results in Table III, it can be stated that data measured by our method agree satisfactorily with those of measured by ICP-AES. Furthermore this comparison shows, that this source seems to be suitable for simultaneous, multielement determination of trace elements in micro volumes of solutions, though the system needs further optimization. One possible way to increase the detection power, is to increase the discharge current. Perhaps it can be carried out by developing another control-sequence, so that higher current values with shorter switch-up time could be applied. In the future we are also planning to increase the number of elements being simultaneously measured, and to analyse other types of samples.

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