The improvement of the detection power
of a U-shaped DC plasma

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Optimization of the operating parameters of U-shpaed DC arc plasma and spectrometer parameters has been undertaken to explore the possibilities of improving its detection power. It is demonstrated, with a U-shaped arc as an example, that the limits of detection, in addition to well-defined parameters as described by Boumans[1,2] and Winge,[3] depend on the signal integration time. It is shown that with increasing integration time, the limits of detection are decreased within some limits and that the precision and concentration sensitivity are improved as well. A mathematical expression for the dependence of the detection limit on the integration time is presented. To increase the reliability of the measurement of the mentioned parameters, the working conditions were optimized for the following analytes: Ag, Al, Au, Cr, Fe, Mn, Ni, Pb, Pd, Pt, and V. The obtained limits of detection are comparable or better than those obtained by ICP for the elements studied. It was estimed that the possibility exists for their further improvement up to 10 times.

Keywords: optical emission spectrometry, signal integration time, detection limits, precision, DC plasma.

INTRODUCTION

The requirements for the detection of low concentrations of various metal elements are continually increasing in various branches of science, technology and environmental studies. For solving the various relevant analytical problems, a lot of laboratory equipment and techniques are commercially available these days. However, there are techniques developed in some laboratories which could be useful for solving the problems as well. It seems that a U-shaped DC arc plasma stabilized with an argon stream is good option for such a task. This arc plasma has been used in some laboratories for analytical work for over twenty years. It has been shown that this arc plasma of-

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fers high emission stability and low limits of detection.[4,5] It has been applied for the determination of various trace elements present in different and complex matrices and natural samples.[6–8] It should be noted that this excitation source is of very simple construction, not expensive, with low running cost and thus available to many laboratories. However, it is possible that its detection power has not been fully utilized, and this investigation was undertaken to find possible ways for its improvement. In this work, by applying an appropriate computer program, the photoelectric recorded analyte signal intensities were accumulated during various exposure times. In this way it was possible to record intensities corresponding to concentrations which could not be detected by the ordinary photoelectric detection.

An optimization of the working conditions preceded the detailed study of the parameters affecting the limits of detection. Since the main feature of this plasma is spatial inhomogeneous emission[9] mainly caused by a demixing effect,[10] the first step of the optimization was the determination of the position of maximal signal-to-background intensity ratio for each element, relative to the arc axis. The second step was the optimization of the entrance and exit slit widths and the entrance slit height, which were carried out using the detection power as the criterion, similar to Boumans.[1] Under the optimum conditions, the following measurements were made for each analyte wavelength (a) standard deviation of blank scatter and (b) sensitivity of the spectral line for various times of integration. From this data, the limits of detection were evaluated.

EXPERIMENTAL

Apparatus

A U-shaped 7.5-ampere arc stabilized by argon vortex, with aerosol supply, was used as the excitation source. The main characteristics of the device have been described elsewhere.[4,9] The total consumption of argon, welding grade, was 3 l/min. The emission was axially viewed from the horizontal, analytical, 3.5 cm long, part of the arc column in the direction parallel to the arc axis. The arc device was mounted on an adjustable carriage, allowing its movement in the direction normal to the optical axis of the spectrometer. The movement mechanism was used to locate the position of the emission peak for each wavelength.

TABLE I. Spectrometer parameters

	200	300	400	500	600
Wavelength/nm	200	300	400	500	600
Diffraction order	13	8	6	5	4
Theoretical resolving power	998400	914440	460800	384000	300000
Dispersion/nm mm^{-1}	0.039	0.070	0.092	0.11	0.14
Practical resolving power 0.2 mm slit width	25600	21400	21700	22700	21400

As a spectrometer, a laboratory modified 2-meter spectrograph PGS-2 with a good quality grating (Bausch&Lomb, 600 grooves/mm, blaze angle 49.5º, width of ruled area 125 mm) and predisperser (Carl Zeiss, Jena) was used. The reciprocal linear dispersion and the other relevant parameters for the wavelength used are listed in Table I. The height of the usable portion of the grating was limited by the spectrograph aperture stop and other construction details to 5 cm thus restricting the aperture ratio to f/30.

The analyte spectral line intensities were photoelectrically recorded (photomultipliers R 106 or R 166) *via* an AD conversion card, ED-300, connected to a PC. Applying the appropriate computer program, the recorded signal intensities were accumulated during the varied exposure times. The measurements were performed for standard and blank solutions.

Solutions

The aqueous solutions of the analytes listed in Table II were pepared from oxides or metals specpure grade from Johnson and Matthey or Spexs. Acids from Merck were used for dissolving and preparing solutions. The stock solutions of 10, 100 and 1000 g/ml were preserved with 0.1 mol/l HCl for the majority of the elements and with 0.05 mol/l HNO_3 for silver. By appropriate dilution of the stock solution, a series of reference solutions was prepared in the range from 1 to 1000 ng/ml. Each of the reference solution contained 0.5 % potassium chloride as spectroscopic buffer and was prepared daily. A Meinhard concentric glass nebulizer, type C, connected with a double-pass spray chamber was used for nebulization of the solution.

PRELIMINARY INVESTIGATIONS

The operating conditions were optimized for elements of different ionization potentials. The lateral relative intensity of the analyte distribution was recorded, and the peak postitions for various elements were determined relative to the arc axis. The position of the arc axis was located as the peak of the continuum emission when a blank solution was nebulized. Since "end-on" observation was used, the distances obtained in this way were taken to be the radii of emission maxima. The emission maxima along with other relevant data are shown in Table II.

TABLE II. Analytes and relevant data

Element	Wavelength/nm	Energy of excitation/eV	Radius of emission maximum/mm	Optimum integration time/s
Ag	328.0	7.57	3.0	30
Al	396.2	5.98	4.0	40
Au	267.6	9.22	2.0	30
Cr	357.8	6.76	4.5	40
Fe	372.0	7.87	3.5	20
Mn	403.1	7.43	3.5	30
Ni	341.5	7.63	3.5	40
Pb	405.8	7.41	3.5	30
Pd	340.5	8.33	2.5	30
Pt	265.9	9.00	2.5	30
V	437.9	6.74	4.0	40

It follows from the data in Table II that the radius of the emission maximum is generally further from the arc axis the lower the first ionization potential of analyte is, although there are some exceptions. For instance, the radius of the peak emission for Al *I* 396.2 nm is expected to be bigger than for Cr *I* 357.8 nm, but experimental observation shows the opposite. It is supposed that the radius of the emission maximum is affected not only by the ionization potential, but, to a lesser degree, by other properties, such as
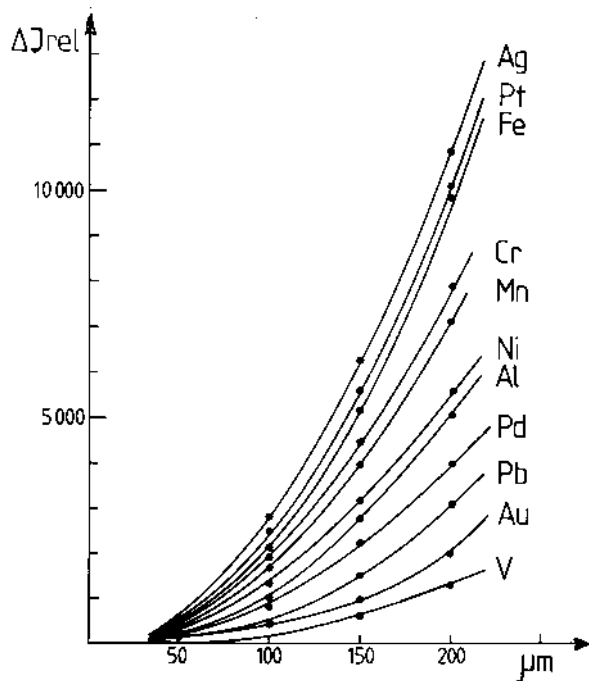
Fig. 1. The dependence of the line net intensity on the slit width.

the stability of the monoxide, the volatility of the aerosol particles and the excitation energy of the spectral line. At the radius of the peak emission, for each element, the dependence of the net line intensity on the width of the monochromator slit was determined, Fig. 1, while the solutions, of 5–50 ng/ml depending on analyte, were nebulized. The largest net signals were obtained with a slit width of 0.2 mm. The analog dependence of the logarithm of the background intensity on the logarithm of the slit width is shown in Fig. 2 for each analyte. These dependencies are similar to those obtained by Boumans[1] for high-resolution monochormators and ICP as the excitation sourse.
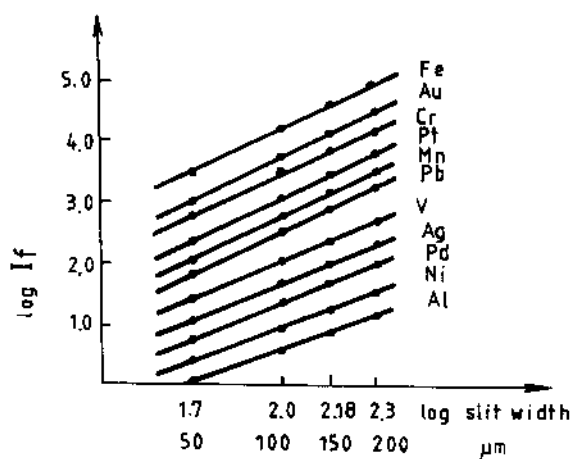

Fug. 2. The dependence of the logarithm of the background intensity on the logarithm of the slit width.
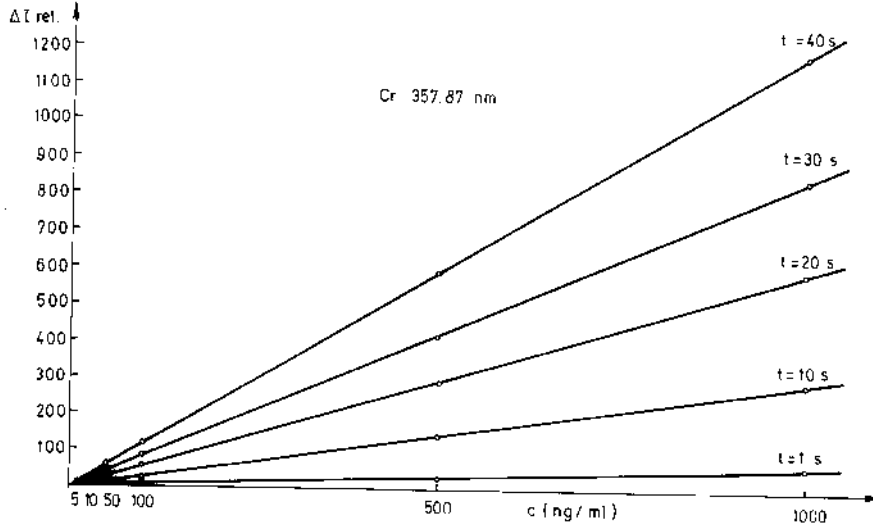
Fig. 3. Calibration curves for Cr *I* 357.87 nm line for the investigated times.

Under the chosen operation parameters, calibration curves of the analyte elements were determined for the integration (*i.e.,* exposure) times of 1, 10, 20, 30 and 40 s. The calibration curves for various integration times for Cr, as an example, are plotted in Fig. 3. From this Figure, it is obvious that the concentration sensitivity (I/c) increases with the integration time, which is expected to increase the precision of the determina-
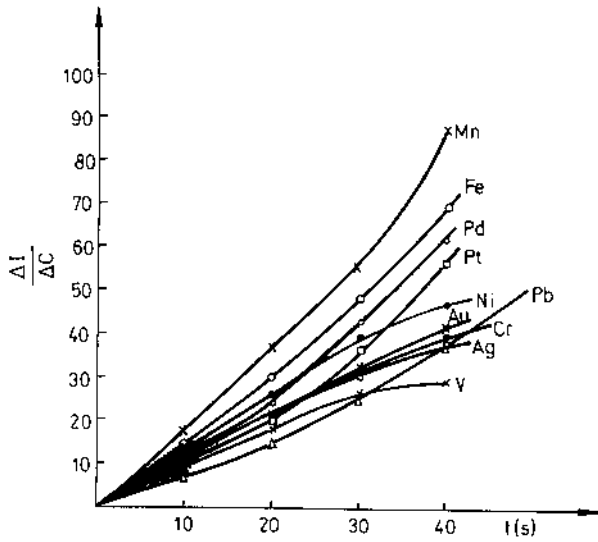

Fig. 4. Dependence of the normalized concentration sensitivity on the integration time for the investigated analytes.

tion. The dependence of the concentration sensitivities, normalized to unity for a one second integration time, are presented in Fig. 4.

A solution containing only 0.5 % of KCl was used for the determination of the background signal and its standard deviation. For each integration time, measurements of the background emission were repeated at least 10 times for statistical evaluation. The detection limit (c_L) is expressed in terms of the signal-to-background ratio (*SBR*), the relative standard deviation $(RSD)_b$ of the background signal and the analyte concentration (c_0) at which the (*SBR*) is measured according to Boumans.[1]

RESULTS AND DISCUSSION

For evaluation of the limits of detection, the following relation was used

$$c_L = k \; \sigma_b/S \tag{1}$$

where c_L is the limit of detection, k is a factor specifing the confidence level (according to Boumans[1,2], $k = 2$), σ_b is the standard deviation of the blank background scatter, and S is the sensitivity (the slope of the calibration curve). By introducing the background intensity, an equivalent relation is obtained

$$c_L = k \, (RSD)_b \, c_0/(SRB) \tag{2}$$

where $(RSD)_b$ is the relative standard deviation of the blank reading, c_0 is the concentration, and (*SBR*) is the signal-to-background ratio at c_0.

The standard deviation of the blank and the sensitivity obtained under optimum working conditions were used to evaluate the limits of detection. The limits of detection plotted against the integradion time are shown in Figs. 5a and 5c. The relative standard deviations, in dependence of the time of integration, are presented in Figs. 5b and 5d. It can be seen that both of these values decrease with increasing integration time. The decrease of $(RSD)_b$, amounts to four to ten times whereas the decrease of c_L is at least ten times, depending on the analyte. It should be noted that both $(RSD)_b$ and c_L for some analytes start increasing slowly after attaining the minimum. A decrese of $(RSD)_b$ with integration time is observed in the range where a shot noise of the detector prevails over the flicker noise of the excitation source. However, for Au, Al, Cr, Ni, Pb and V a minimum is not reached up to a 40 s integration time. This means that the signal integration time is not long enough to detect the inflection point on the curve. These curves could be used to estimate the optimum integration time for this experimental set up. For instance, for iron, there is no use of employing an integration time longer then 20 s, while for most of the other analytes the optimum time is about 30 s. However, for analytes where a minimum is not attained, some lowering of c_L could be expected by further extending the integration time, but times longer then 40 s were not used for practical reasons. A shorter integration time could be used if the ultimate low limits of detection are not required, or if the volume of the analyzed solution is limited. For a 40 s integration time and three readings at least 3 ml of solution with the type C Meinhard concentric glass nebulizer.
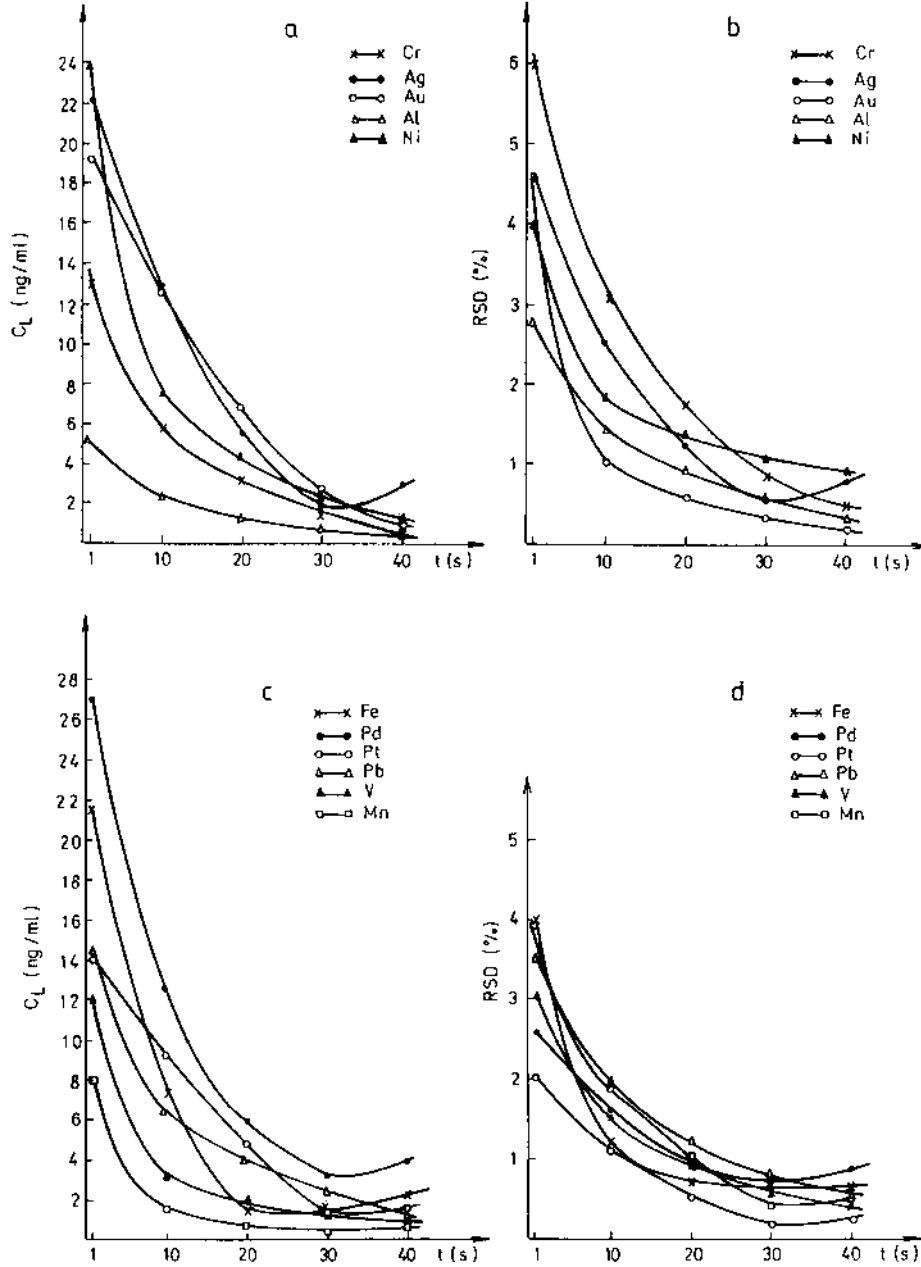
Fig. 5. Limits of detection and relative standard deviation of the background: a and c – dependence of the limits of detection on the time of integration; b and d – dependence of the relative standard deviation on the time of integration at the analyte wavelengths for the investigated analytes.

On the basis of the obtained results, an attempt has been made to establish a mathematical relation for the dependence of the limit of detection on the integration time. It was found graphically that the relation

$$c_L \sim \frac{c_L^0}{\sqrt{t}} \qquad (3)$$

where c_L^0 is the limit of detection for a 1 s integration time, and t is the time of integration, fits approximately the decending parts of the experimentally obtained curves in Figs. 5a and 5c. This relationship indicates that the noise in the region considered is caused mainly by shot noise, and that the relation given by Eq. (3) ceases to be valid when flicker noise becomes dominant. The comparison between the experimental values and those calculated according to the proposed Eq. (3) is illustrated for Ni and Cr (as examples) in Fig. 6.
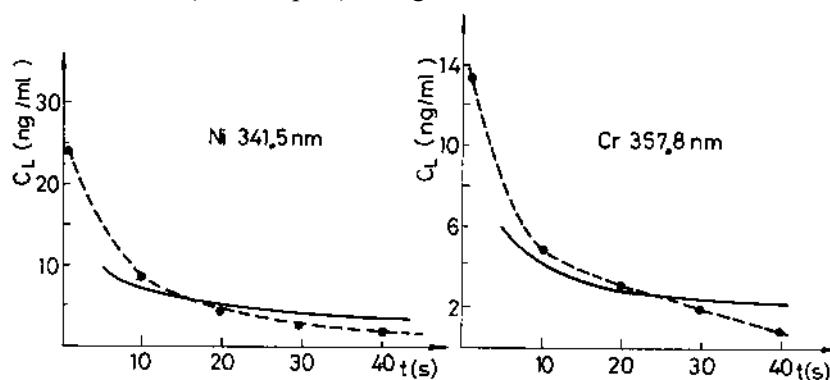

Fig. 6. Dependence of the limits of detection on the integration time for Ni and Cr obtained by experimental measurements, dashed line and calculated according to Eq. (3), solid line.

TABLE III. Limits of detection (ng/ml) compared with other plasma sources

Element	This work	ICP-AES[11]	DSP-AES[11]	ICP-MS[11]
Ag	1.7	3.0	3.7	0.2
Al	0.4	20.0	2.0	0.6
Au	0.9	10.0	2.0	0.6
Cr	0.8	4.0	2.0	0.2
Fe	1.4	3.0	3.0	–
Mn	0.3	0.6	2.0	3.0
Ni	1.2	8.0	2.0	0.2
Pb	1.3	30.0	10.0	0.3
Pd	3.0	30.0	2.0	–
Pt	1.3	40.0	26.0	–
V	0.9	2.0	2.0	0.5

The limits of detection evaluated from measurements with the optimum integration time compared with those published for other plasma sources are shown in Table III. It can be seen that the obtained limits of detection compare favorably to those obtained using ICP-AES, DCP-AES and, for two analytes, ICP-MS as well. In the other words, with this method and using a simple excitation source, it is possible to obtain results similar to or better than those obtained with much expensive equipment. Also possibilities for further improvement, discussed below, exist.

It should be noted that for the optimum limits of detection, a rather wide monochromator slit and a long integration time are required. The wide slit (0.2 mm) compensates for the low throughput of the monochromator for the small aperture ratio and for the low emission intensity of the U-shaped DC plasma. Emission of the analyte spectral lines occurs in the fringe region where the temperature is lower than in the analytical zone of the ICP, and thus lower emission intensities are obtained. However, it seems that an analyte reaches close-to-optimum temperatures for the emission of atomic lines. Consequently, as a rule, the bigger radius of the peak emission the longer the required integration time is.

Further improvement of the limits of detection could be expected if a monochromator with a bigger throughput and at the same time with a higher resolution were used. Such a monochromator would allow the narrower slit to be used, which would produce a higher signal to background ratio and, at the same time, retain a high intensity of the background and thus a low $(RSD)_b$ limited by flicker noise only. According to Eq. (2), this would result in a lowering of the limits of detection for the plasma studied in this work. A rough estimation shows that with a better monochromator a further lowering of the limits of detection by up to ten times could be expected.

CONCLUSIONS

From the results obtained in this work, it can be concluded that the integration time essentially influences the concentration sensitivity and, consequently, the limits of detection and precision of determination. With the described spectrometer and optimized operating conditions, the majority of the obtained limits of detection compare favorably to those of ICP-AES and DCP-AES. It was also shown that with further optimization of the spectrometer, primarily by employing a monochromator with a bigger throughput, additional improvement of the detection power, by up to ten times, is possible.

A mathematical equation was proposed which describes the dependence of the limits of detection on the integration time if shot noise prevails. This allow an estimation of the limits of detection for any analyte if the corresponding value for a 1 s integration time is known.

It could be useful to investigate influence of the analyte signal integration time on the detection power in the case of other excitation sources in conjunction with high-resolution spectrometers.

И З В О Д

ПОБОЉШАЊЕ МОЋИ ДЕТЕКЦИЈЕ ЛУКА U-ОБЛИКА

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Оптимизовани су радни параметри лука U-облика као и параметри спектрометра како би се испитале могућности за побољшање моћи детекције лука. Показано је да граница детекције зависи поред већ дефинисаних параметара[1,2] и од времена интеграције сигнала. Са повећањем времена интеграције граница детекције опада, што је изражено математичком зависношћу. Побољшани су и прецизност мерења као и концентрациона осетљивост. Мерења су извршена под оптималним условима за следеће елементе: Ag, Al, Au, Cr, Fe, Mn, Ni, Pb, Pd, Pt и V. Добијене границе детекције су упоредљиве или боље од оних добијених применом индуктивно спрегнуте плазме.

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REFERENCES

1. P. W. J. M. Boumans, J. J. A. M. Vrakking, *Spectrochim. Acta* **39B** (1984) 1261
2. P. W. J. M. Boumans, J. J. A. M. Vrakking, *Spectrochim. Acta* **40B** (1985) 1085
3. R. K. Winge, V. J. Peterson, V. A. Fassel, *Appl. Spectroscopy* **33** (1979) 206
4. M. Marinković, V. G. Antonijević, *Spectrochim. Acta* **35B** (1980) 129
5. M. M. Kuzmanović, M. S. Pavlović, M. Marinković, *Spectroscopy Lett.* **29** (1996) 205
6. J. S. Dobrosavljević, V. G. Antonijević, *Glasnik Hem. društva Beograd* **43** (1978) 613
7. N. Daskalova, N. Krasnobaeva, S. Velichkov, B. Pavlović, M. Marinković, *J. Serb. Chem. Soc.* **56** (1991) 205
8. M. Tripković, M. Todorović, I. Holclajtner-Antunović, *Anal Chim. Acta* **296** (1994) 315
9. G. Malović, M. Tripković, I. Holclajtner-Antunović, *Contrib. Plasma Phys.* **34** (1994) 777
10. M. S. Pavlović, M. Marinković, *Spectrochim. Acta* **53B** (1998) 81
11. L. H. J. Lajunen, *Spectrochemical Analysis by Atomic Absorption and Emission*, Royal Society of Chemistry, Cambridge, 1992.