

METAL TRACE ANALYSIS BY FLAME/GRAPHITE FURNACE
OG SPECTROSCOPY

I.V. Bykov, A.B. Skvortsov, Yu.G. Tatsii and N.V. Chekalin*

*V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry,
USSR Academy of Sciences, Moscow, U.S.S.R.*

Résumé - A l'aide de différents schémas d'excitation la détection optogalvanique des traces d'éléments a été effectuée dans des solutions d'eau pure ainsi que dans des matrices complexes par atomisation des échantillons dans une flamme et un four électrothermique en graphite.

Abstract - The optogalvanic detection of trace elements with various excitation schemes is investigated for pure water solutions and for matrix in flame and electrothermal graphite furnace.

In the reviews /1-3/ the perspectives of optogalvanic detection of atoms in flames were shown for trace element analysis. Now it is important to investigate the possibilities of the method more carefully and to find the ranges of its optimum application. In this work we studied various optical schemes of excitation of Na, In, Cs, Yb atoms in air-acetylene flame and determined the conditions of effective ionization of atoms in water solutions and in matrix. The matrix interferences were investigated for In in SnCl₂ and SnSO₄ matrices and for Cs in NaCl matrix. The experiments with the electrothermal graphite furnace are also described.

Experimental Apparatus. The experimental apparatus is schematically shown in fig. 1. Two various systems were used as excitation sources: 1) dye lasers with a prism telescope pumped by N₂-laser; 2) grazing incidence dye lasers, pumped by the second harmonic of Nd-YAG laser. The dye laser radiation was amplified and could be doubled in KDP crystal. The main characteristics of both laser systems are shown in table 1. An air-acetylene flame was used as a source of free atoms.

Table 1 Characteristics of lasers used

	Nd-YAG laser (532 nm)	Grazing inci- dence dye laser	2nd harmo- nic of dye laser	N ₂ -la- ser 337 nm	Dye laser with prism telescope
Pulse energy E_p, mJ	10	0.1-1.0	0.05-0.1	4	0.03-0.1
Pulse dura- tion τ_p, ns	15	13	11	8	5
Line width $\Delta\lambda, \text{cm}^{-1}$	-	0.35	-	-	0.5
Repetition rate f, s^{-1}	2-50			1-12	

*Mr. Chekalin was unfortunately unable to come to the Colloquium but has written the lecture he would have presented which is published in the Proceedings.

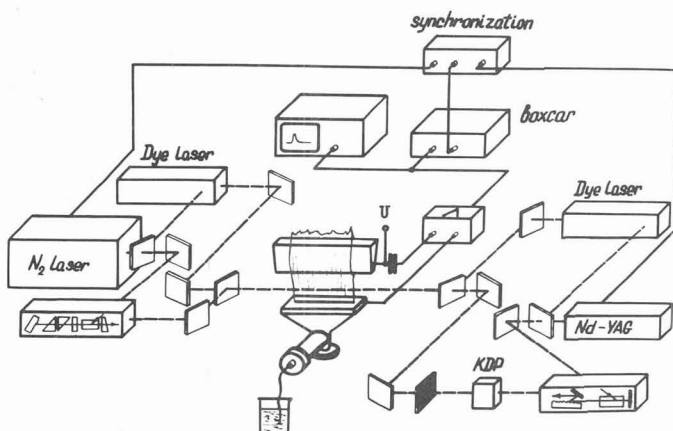


Fig. 1 - The experimental apparatus.

Dissolved samples were aspirated into a standard premix slot burner 11 cm long. Two collimated dye laser beams were directed collinearly along the burner axis by a system of mirrors. The ions arising in the radiated zone were collected on the watercooled stainless steel electrode, being under the negative potential ($-800 - -1200$ V). The electrically grounded burner head served as an anode. The electrode had a form of parallelepiped $4 \times 20 \times 120$ mm and could be placed either in the flame, or on one side of the flame. Ion current pulses were removed from the capacitance electrode - burner head (~ 25 pF), then they preamplified and after passing through the cut-off HF filters were observed on the C-1-70 oscilloscope or processed with a box-car averager, having 1μ s gate width. The time constants of the filters provided the integrating of input signals.

Results and discussion. The excitation schemes for elements used and corresponding detection limits (DL) (36 criteria) are given in Table 2. Let us consider the results for particular atoms in more detail.

Indium. The schemes of excitation are shown on fig. 2. To compare various excitation-ionization schemes we can, besides of DL, use the efficiency of ionization, determined as a part of exciting atoms N^{ex} converted into ions. When the optical saturation was reached, the N^{ex} number could be easily estimated. When there were no optical saturation we could get only the lower estimation of γ .

For one-step excitation ($\lambda = 303.9$ nm) the ΔE value (see Table 2) is much higher than $kT = 0.22$ eV. Yet the efficiency of ionization from $5d^2D_{3/2}$ level and $5d^2D_{5/2}$ level, which is probably in equilibrium with the former is high enough ($\sim 4\%$) and provides the low DL for this scheme. The cross-section of a laser beam in which the optical saturation was reached is 0.08 cm, but as one can see from fig. 3, the cross-section of the flame in which atom concentration is substantial is much larger. The use of more powerful lasers will result in the significant lowering of DL in this case.

Note that DL on $\lambda = 303.9$ nm for $\tau_p = 11$ ns (this work) are nearly equal to DL for $\tau_p = 800$ ns from CMX-4 flash-lamp laser /3/, in spite of the fact that τ_p values differ more than 70 times. It would be more correct, of course, to compare the efficiency of ionization, but it is impossible to do on the basis the data /3/.

Table 2. The experimental conditions and results obtained

Element	$\alpha \cdot 10^2$	E_i eV	Excitation scheme	λ_1 nm	λ_2 nm	\mathcal{E}_1 μJ	\mathcal{E}_2 μJ	τ_p ns	E eV	DL pg/ml	
In	8.5	5.78	$5p^2P_{1/2}^0 - 5d^2D_{3/2}$	303.9	-	70		11	1.7	7	
			$5p^2P_{3/2} - 6s^2S_{1/2} - 8p^2P_{1/2}^0$	451, 1	572.8	27	65			0.6	3
			$8p^2P_{3/2}^0$		571.0	27	65		5	0.6	1
			$5p^2P_{3/2} - 6s^2S_{1/2} - 9p^2P_{1/2}$	451.1	526.3	30	52		5	0.4	10
Cs	2	3.89	$9p^2P_{3/2}$		525.4	30	52		0.4	3	
			$10p^2P_{1/2}$	451.1	502.3	30	47	5	0.3	30	
Yb	-	6.25	$10p^2P_{3/2}$		501.8	30	47	5	0.3	7	
			$6s^2S_{1/2} - 7p^2P_{3/2}$	455.5	-	120	-	5	1.17	2	
Na	100	5.14	$4f^{14}(^1S)6s^2 - 4f^{14}(^1S)6s6p - 4f^{13}(^2F_{7/2}^0)6s^26p_{3/2} - \text{AI level}$	555.6	581.2	200	500	13	-0.25	100	
			$3s^2S_{1/2} - 3p^2P_{1/2} - 4d^2D_{3/2}$	589.6	568.2	35	35	5	0.86	1	
			$3p^2P_{3/2} - 4d^2D_{3/2, 5/2}$	589.0	568.8	35	35			0.6	

α - efficiency of atomization in acetylene-air flame; E_i - energy of ionization;
 $\Delta E = E_i - E^{ex}$; DL - limit of detection; \mathcal{E}_1 and \mathcal{E}_2 - laser pulse energies for 1st and 2nd steps; τ_p - the time width of laser pulse.

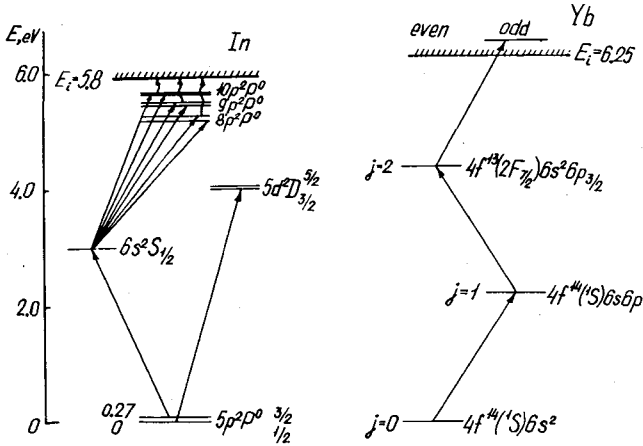


Fig. 2 - The schemes of excitation for In and Yb.

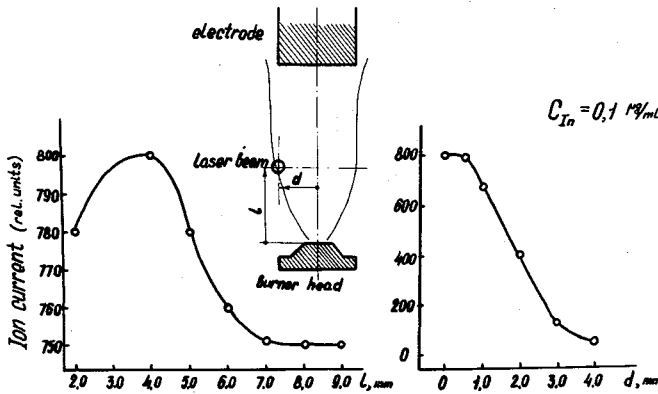


Fig. 3 - Space profile of In atoms distribution in air-acetylene flame, obtained by monitoring the laser beam ($\lambda = 303,9$ nm) over the flame and detecting the arising ions. The electrode-burner head distance is 11 mm.

In two-stepped schemes we investigated the excitation of In atoms on 8p, 9p and 10p levels with a corresponding diminution of ΔE values (see table 2). We could not reach the optical saturation of these levels - it was reached only for the first step of excitation (fig. 4). Under these experimental conditions we don't observe the increase of the analytical signal with a growth of excitation level. It is difficult to compare the population of exciting levels without saturation, but the estimation of ionization efficiency for $8p^2P_{3/2}$ level brings to $\gamma \approx 0.8$ (we suppose that there is no mixing between $5p^2P_{1/2}$ and $5p^2P_{3/2}$ levels during the laser pulse $\tau_p = 5$ ns, and that $8p^2P_{3/2}$ level is in saturation. We also suppose that the efficiency of atomization for In is 0.085). It is clear that even for $\Delta E = 0.6$ eV the exciting level is in equilibrium with the continuum system of levels. A further rise of the excitation level is effect-less, because transition probabilities fall quickly with n (level number). So, the $8p^2P_{3/2}$ level is optimum for this two-step scheme and provides minimum DL. It is interesting to estimate for this case the minimum detected number of atoms and ions. Using the expression

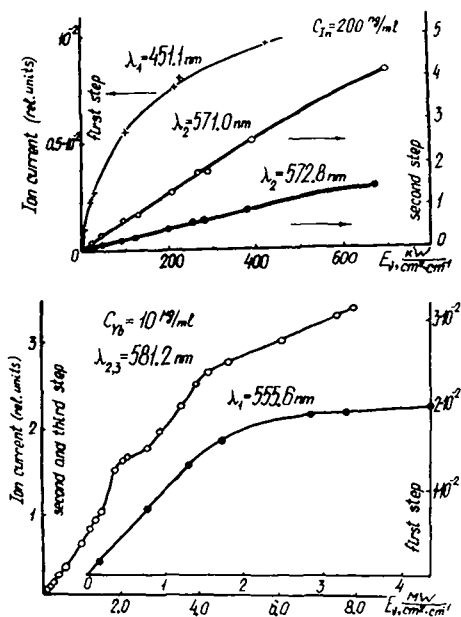


Fig. 4 - Saturation curves for In and Yb.

for atom concentration in flame from /4/ we found that minimum ion number is ~ 100 , minimum atom number ~ 250 and minimum detected concentration $\sim 5 \cdot 10^3 \text{ cm}^{-3}$ for our experimental conditions.

As one can see from fig. 4 different analytical signals were observed from doublet components $8p^2P_{1/2}$ ($\lambda = 572.8 \text{ nm}$) and $8p^2P_{3/2}$ ($\lambda = 571.0 \text{ nm}$). The ratio of this signals is equal to 2.8 for this doublet. Analogous results were also obtained for $9p$ and $10p$ doublets. It is evident that the rates of collisional mixing of the components are less than τ_p^{-1} but what mechanisms bring about the ratio observed, is not clear. This problem is now under consideration.

Ytterbium. The excitation scheme is shown on fig. 2. In this scheme except of collisional ionization from $4f^{13} (2F_{7/2}) 6s^2 6p_{3/2}$ level (two-step excitation), the radiative transition is also possible from this level to autoionizing (AI) level with $E = 6.5 \text{ eV}$. The wavelength of this transition coincides with the second step wavelength (581.2 nm) so only two dye-lasers are needed for such three-step excitation. In general this scheme is more complex and demands the use of three lasers, but it provides higher selectivity and rate of ionization. This scheme can be used when collisional ionization is ineffective. For Yb atom this scheme provides a low DL-0.1 ng/ml in spite of the fact that atomization of YbCl_3 in air-acetylene flame is very poor. The excitation conditions are near the optimum - the optical saturation having been reached in all three steps. The estimated cross-section of AI transition is $\sigma_{AI} \sim 10^{-16} \text{ cm}^2$.

Sodium. The minimum detected concentration is limited by blank (Na contamination in deionized water being ~ 10 ng/ml). The DL obtained by extrapolation of a signal to noise level is low enough, being less than 1 pg/ml for two-step excitation. The optical saturation is reached easily for both steps. The linear part of calibration curve extends to 3 μ g/ml. For higher concentrations the nonlinearity appears due to the space charge effects. The space charge brings about the broadening of the excitation spectra and ion current pulses /6/. The broadening of the laser pulses can be used for control of the effect.

Note, that various two-step excitation schemes (through the $3p^2P_{1/2}$ and $3p^2P_{3/2}$ levels - see table 2) provides different magnitudes of analytical signals. This fact shows, that mixing time for these levels in flame is more than $\tau_p = 5$ ns.

Caesium. The one-step excitation was used and the optical saturation was reached. The efficiency of collisional ionization from $7p^2P_{3/2}$ level is very high (~ 1.0) and in spite of large ΔE value and low efficiency of atomization of Cs in air-acetylene flame ($\sim 2\%$) the DL is the same as in /5/ for propane-butane-air flame.

The matrix interferences. The low DL in water solutions doesn't guarantee the low DL in real samples where matrix interferences occur. We investigated the determination of In in presence of Sn having high ionization potential and influence of Na on analytical signal of Cs. For In-Sn system the matrix interferences depend on the excitation scheme. The solutions of SnCl_2 and SnSO_4 in 1 M acids were used.

A. One-step excitation ($\lambda = 303.9$ nm). For SnCl_2 solutions the continuous background was observed in the entire tuning range of the dye used (285-310 nm). The magnitude of this background depends to a large extent on a potential U of electrode - it rises as U^6 and then is saturated. The second interference factor is suppression of selective In signal when matrix concentration arises (fig. 5). For 10 g/l of Sn the signal of In drops to 30%, and when Sn concentration arises it is completely recovered. As a result of these interferences the DL of In in SnCl_2 solution (10 g/l Sn) is 1500 times higher than it is in water solution. The nature of continuous background is unknown. It may be connected with large quantities of SnCl_2 molecules in flame as only about 4% of molecules are atomized. The wide UV absorption band of these molecules overlaps the tuning range of the dye laser and multiphoton ionization is possible. Even if the efficiency of this process is 10^{-7} this is quite enough to provide the observed amplitude of the background. The SnCl_2 can also serve as the effective quencher of exciting In atoms and brings about suppression of the analytical signal. For SnSO_4 molecules the continuous background is absent.

B. Two-step excitation. The matrix interferences are much smaller in this case (fig. 5). For SnSO_4 the suppression of the analytical signal only about 10% was observed up to Sn concentration 10 g/l. This suppression rises to 15% for 45 g/l Sn. For SnCl_2 solutions the suppression is higher - up to 25%. No continuous background is observed. The calibration curves for pure In solutions and for (In + 10 g/l Sn) solutions are given in Fig. 6.

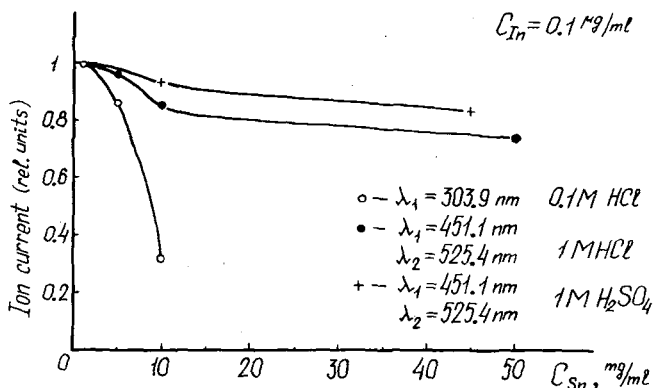


Fig. 5 - The matrix interferences in In-Sn system.

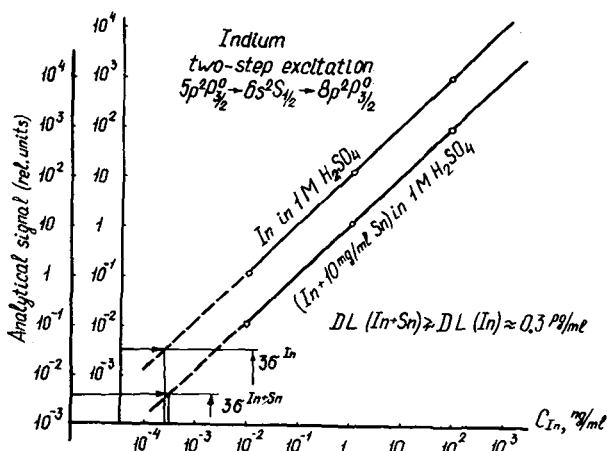


Fig. 6 - The calibration curves.

The curves are parallel and DL for water solutions and matrix are practically equal. This provides the determination of In trace in Sn up to $10^{-8}\%$. The samples of Sn, which we investigated so far, had In contamination $\sim 10^{-5}\%$. The real measurable concentration of In are limited in our experiments by burner "memory" and are equal to 10 $\mu\text{g/ml}$ - more than order of magnitude higher than DL.

Cs+Na system. Both atoms effectively ionize in flame, creating the space charge near the electrode. The range, where Cs analytical signal can be detected, diminishes, when Na concentration increases. This effect depends on the electrode configuration and its position in flame (see also /3/). In our experimental conditions the analytical signal from 20 ng/ml Cs independent on Na was observed up to 1 $\mu\text{g/ml}$ Na. In concentration range 1-200 $\mu\text{g/ml}$ Na the 18% increase in signal was observed. The further Na concentration increase gives rise to suppression of Cs signal (for 2.10⁴ $\mu\text{g/ml}$ the Cs signal dropped to 10%).

Experiments with flameless atomizer. The first attempt of optogalvanic detection with graphite crucible was reported in /7/. We used two modifications - the graphite crucible and graphite furnace

HGA-72. The configuration of apparatus is presented in fig. 7. For graphite crucible the stainless plate was used as a electrode at the

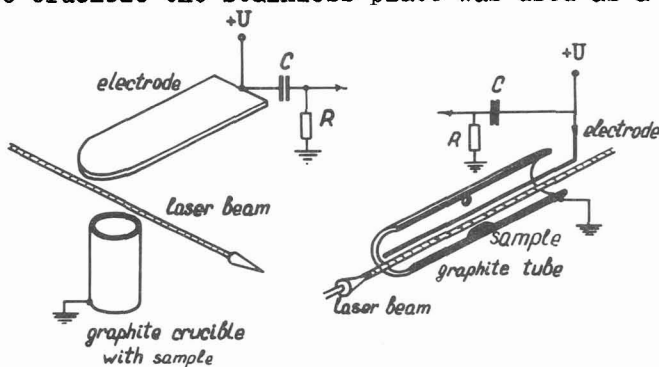


Fig. 7

distance 4 mm above crucible. The laser beams propagated 4 mm above crucible near the electrode not touching it. The signals were observed for positive and negative potential up to 1 kV. The experiments were carried in air (the crucible being changed after 2-3 experiments) and nitrogen atmospheres.

For graphite tube the tungsten rod (diameter 1 mm) along tube axis was used as anode. The laser beams propagated along the rod. Maximum potential on the rod in that case was less than 300 V to avoid the breakdown between rod and furnace. The volume of the sample to be analysed was 20-30 μ l. The experiments were carried out in gas-stop mode, in argon atmosphere.

The Na, Cs, In, Yb water solutions were investigated with one-step and two-step excitations. It was found the analytical signal to be 10-100 times higher, compared to flame atomization, but the precision was not very good. Evaluated absolute detection limits of Na and In are 10^{-14} - 10^{-15} g, and practically there is no memory effect. The results obtained are promising but it is necessary to improve precision for real samples analysis.

References

- /1/ TRAVIS J.C., TURK G.C., GREEN R.B. Anal. Chem. 54 (1982) 1006A.
- /2/ ZOROV N.B., KUZYAKOV YU.YA., MATVEEV O.I. Zh. Anal. Khim. 37 (1982) 520 (Sov.)
- /3/ TURK G.C., TRAVIS J.C., DE VOE J.R., O'HAVER T.C. Anal. Chem. 51 (1979) 1890.
- /4/ OMENETTO N., WINEFORDNER J.D. Progr. Anal. Atom. Spectr. 2 (1979) 1.
- /5/ ZOROV N.B., KUZYAKOV YU.YA., CHAPLYGIN V.I. Zh. Anal. Khim. 38 (1983) 802 (Sov.)
- /6/ VAN DIJK C.A., CURRAN F.M. LIN K.C. GROUCH S.R. Anal. Chem. 53 (1981) 1275.
- /7/ GONCHAKOV A.S., ZOROV N.B., KUZYAKOV YU.YA., MATVEEV O.I. Zh. Anal. Khim. 34 (1979) 2312 (Sov.)