On the Sensitivity of Direct Spectral Analysis of Solutions

SEPPO WILSKA

Department of Chemistry, Finland Institute of Technology, Helsinki, Finland

During an investigation of trace elements in Finnish ground- and mine waters, the author has attempted to find the most suitable method with regard to sensitivity, accuracy and speed using the available apparatus. It is evident that, when numerous trace elements, as many as possible, are to be determined, the spectral analysis has all advantages when compared *e. g.* with the most frequently used colorimetric methods. The spectral method chosen by the author for direct analysis of dilute solutions and a study concerning the sensitivity obtained by this method compared with other methods will be presented in this paper.

Since the classical publication of Lundegårdh [1] much research work has been made to find out a suitable method for direct spectral analysis of solutions. Several sources of excitation have been experimented. On the basis of the pioneering work of Lundegårdh on the flame spectrographic analysis, many, especially European scientists have used the flame exctitation either alone or combined with spark, as did Bouchetal de la Roche [2]. Of American investigations those of Cholak and Hubbard [3] on spectral analysis with the air-acetylene flame and the recently published work of Gilbert, Hawes and Beckman [4] on the use of Beckman flame spectrophotometer are to be mentioned. The modern flame photometry is the best technique for many purposes, but the chief limitation of this method is that several important elements either cannot be excitated by the flame or have too weak an emission, consequently cannot be determined or have a very low sensitivity.

Thus, the analysis of solutions by pure spectrographic means has further been of continued interest. Many investigators have not carried out the analysis in liquid phase. Fred, Nachtrieb and Tomkins [5] and many others dried drops of solution on the electrodes before excitation. Sloviter and Sitkin [6] impregnated the electrodes with the solution to be analysed and Roux and Husson [7] determined boron by impregnating a cotton pad with the solu-

tion and burning this between the electrodes. Duffendack, Wolfe and Smith [8] and later Duffendack, Wiley and Owens [9] instead of drying used excitation between a solid electrode and the free surface of a liquid, and this procedure has won many supporters. Lundegårdh (*l.c.*) proposed, according to Necke the continous feeding of solution into the analytical gap through a hollow upper electrode, and this method has been further developed by Keirs and Englis [10]. A spark excitation is used between two liquid surfaces in the "dropping electrode" of Lomakin [11] and on the other hand between a solid electrode and a thin film of solution in the method of Rohner [12]. Already Hartley [13] produced the spark from a thin liquid film by taking advantage of the capillarity.

None of these methods seemed to have the characteristics required for the work at hand. The residue methods, even though sensitive enough, were not convenient for very dilute solutions, as the nature waters are, and the continous feeding method lacked the simplicity and sensitivity desired. The "Porous Cup Electrode Technique", a very simple and ingenious continous feeding method by Feldman [14], however, seemed to fulfill all reasonable requirements. The sensitivities given by Feldman were in most cases rather high, in some cases, however, striking low. Therefore, the sensitivity of this technique was at first studied by means of the available apparatus.

Feldman (*l. c.*) uses as the upper electrode a spectrographic graphite rod 0.6 cm in diameter and 3.75 cm in length, drilled along the axis with 0.125-inch drill from one end to within 1.1 ± 0.2 mm from the other end adjusting the drill press with a special jig. The lower electrode is a graphite rod, 0.125 inch in diameter with a flat or pointed end. The solution to be analysed is inserted into the upper electrode by means of a long-nosed pipette and feeds to the analytical gap trough the intact bottom of the rod. There it is dispersed and excited by the high-voltage spark from a Baird spark source with a synchronous interrupter, or by a low-voltage intermittent arc. A single filling, of about 0.32 ml, will permit an exposure of 120 to 240 seconds. Usually exposures of 180 seconds are made. A 5—10 second pre-spark period followed by a rest period is proposed. Sensitivity limits for 45 elements in 10 % sulfuric acid solution (Pb, Ba and Sr in 3 % nitric acid) are given. A preferential adsorption of trace elements by the graphite is not detected. Duplicate samples have given intensity ratios agreeing to within 2 to 5 % of their mean. The analytical accuracy has not yet been systematically estimated by independent methods. No noticeable vertical variation of intensity in the source is observed.

EXPERIMENTAL

English „Ship Carbons", 7 mm in diameter, were used as electrode material. The carbon rods were ignited according to the usual procedure of our spectrographical laboratory 75 seconds by a current of 300 amperes in air to remove impurities. After this treatment the carbons were 6 mm in diameter, very porous and still contained as contaminations much boron, thus indeterminable by means of these electrodes, and traces of Mg, Ca, Si and Ti, which therefore are not considered in this work. The electrodes were like those of Feldman, only the lower end of the drilling was not conical as usually made by a drill, but flat. The purpose of this was to obtain a more equal feeding of solution trough the bottom. A special drill press with a jig was not needed, but the electrodes could be made with a sufficient speed in a lathe by a 3 mm drill, fitted with a steel collar equipped with a set screw at a distance of 3.65 cm from the point of the drill. A flat-pointed carbon rod 3 mm in diameter at the point was used as the lower electrode.

Dilution standards of the elements were made by using reagent grade elements or compounds. As solvent 3 % nitric acid, purified by distillation, was used in most cases, only few elements were analysed in 10 % sulfuric acid solution. In contrary to Feldman the observation was made that a nitric acid solution feeds to the analytical gap much better than a solution in 10 % sulfuric acid, which had in many cases a too weak wetting power, which could be helped only by a wetting agent.

The commercial type of Feussner spark source, made by Heraeus GmbH, Hanau, was used with synchronous interrupter and a resistance of 40 ohms. The full capacitance, $3.33 \times 10^{-3} \mu f$ and the inductance marked 1/10 giving the value 8×10^{-6} henry were used. As it can be seen, the most sparklike conditions were effected in order to obtain particularly the spectra of singly ionized atoms.

A Zeiss Qu 24 Spectrograph with a useful wavelength range from 2 200 to 4 600 Å was used. It had a pre-slit optical system consisting of a condenser $f = 80$ cm, a field aperture with horizontal slits of different widths and a lens $f = 160$ cm which formed an image of the condenser on the slit of the spectrograph. The optical system was set sharp for 3 000 Å and left fixed. A slit width of 0.025 mm was used. The exposure time was 180 seconds after a 15-second pre-spark period, the analytical gap 2 mm. Kodak Scientific Plates III-O were used, developed in a 1 : 2 diluted Kodak D-19b developer 3 minutes at a temperature of 18° C, rinsed in a stop bath, fixed in Kodak F-5 fixing bath, washed and dried in air.

The sensitivity limits for different elements are given in Table 1, in the first sensitivity column those of the author, in the second are the figures of Feldman [14], thereafter the values of Cholak and Hubbard [3] by the air-acetylene flame method and in the last column those by Gilbert et alii [4] by Beckman flame photometer.

Thus all elements investigated by the author have been detected in a concentration below 100 ppm, and a great majority has the detection limit 10 ppm or even less. The flame photometer is much more sensitive when alkalies are to be determined, in all other cases the PCE-technique either equals to or exceeds the flame photometry in sensitivity.

DISCUSSION

When comparing the Raies Ultimes of different elements obtained with this technique with those collected by Meggers [16] in a table comprising the

Table 1. Sensitivity limits for different elements in the direct spectral analysis of solutions.

Ele-ment	Raie ultime *			Approximative sensitivity ppm			
		Classi-fication	Total excitation potential	PCE-technique		Flame excitation	
	λ			Author	Feldman	Cholak	Gilbert
Ag	3280 . 683	I	3.8	0.02	1	5	2
Al	3961 . 527	I	3.1	0.5	1		No emis-sion
As	2349 . 84	I	6.6	3			
	2288 . 12	I	6.7	3			
	2780 . 197	I	6.7	10	100		
Au	2427 . 95	I	5.1	30			
	2675 . 95	I	4.6	100	100		
B	2497 . 733	I			0.5		5
Ba	2335 . 269	II	11.2	0.5		100	1
	2304 . 235	II	11.2	0.5			
	4130 . 664	II	10.9	4	50		
Be	3130 . 416	II	13.2	0.02			
	2348 . 610	II	5.4	0.02			
	3131 . 072	II	13.2	0.05	0.02		
Bi	3067 . 716	I	4.0	1	5		
Cb	3094 . 183	II	8.0		5		
Cd	2265 . 017	II	14.4	0.2	100	200	500
	2288 . 018	I	5.4	0.2			
Ce	4012 . 388	I	> 8.7	10			
	3942 . 736	II		35	25		
Co	2286 . 156	II	14.3	0.5		1	5
	2363 . 787	II	14.2	0.5			
	3453 . 505	I	4.0	2	2		
Cr	2835 . 633	II	12.6	0.3		0.5	3
	2843 . 252	II	12.6	0.3	2		
Cu	3247 . 540	I	3.8	0.2	0.6	0.5	f
Cs	8521 . 10	I	1.4		15	50	0.1
Fe	2382 . 039	II	13.0	0.5		5	10
	2395 . 625	II	13.0	0.5			
	2599 . 396	II	13.0	0.5	2.5		
Ga	2943 . 637	I	4.3	10	10		1
	4032 . 982	I	3.1	10	10		
Ge	3039 . 064	I	4.9		10		
Hf	2820 . 224	II	9.2		4		
Hg	2536 . 519	I	4.9	10	50	200	50
K	4044 . 140	I	3.1		200	8	0.05

* Data according to Harrison [15]. In flame methods these lines are not necessarily used·

Table 1 (cont.)

In	3256 · 090	I	4.1		10	1
La	3949 · 106	II	9.1	1	5	
Li	3232 · 61	I	3.9	10		0.1	0.05
	6707 · 844	I	1.8		0.1	
Mg	2795 · 53	II	12.0		0.01	5	10
Mn	2576 · 104	II	12.2	0.02		0.3	1
	2593 · 729	II	12.2	0.05	2	
Mo	2816 · 154	II	11.9	1		
Na	3302 · 323	I	3.7	35	35	0.2	0.01
Ni	2287 · 084	II	14.8	4		10	3
	3414 · 765	II	14.2	4	10	
P	2535 · 65	I	7.2	5	80	No emission
Pb	2833 · 069	I	4.4	4	10	100	300
Pt	2659 · 454	I	4.6	1	100	
Pd	3404 · 580	I	4.4		2	50
Re	3460 · 47	I	3.6		10	
Ru	3498 · 942	I	3.5		100	30
Sb	2598 · 062	I	5.8	3	100	No emission
Sn	2839 · 989	I	4.8	5	100	500
Sr	4077 · 714	II	8.7	0.2	0.5	0.2	0.5
Te	2385 · 76	I	5.8	10	1 000	
Th	3538 · 75		> 3.5	35		
	3290 · 59		> 7.31		100	
Ti	3349 · 035	II	11.1		3	
Tl	2767 · 87	I	4.5	3		0.4	1
V	3033 · 822	II		0.3		
	3093 · 108	II	11.2	1	5	
W	2397 · 091	II	> ·10.9	3		
	4008 · 753	I	3.4	30	500	
Y	3710 · 290	II	10.0		0.1	
Zn	3345 · 020	I	7.8	4	25	3 000	No emission
Zr	3391 · 975	II	10.7	1		
	3273 · 047	II		3	2	

strongest lines of the second spectra of elements, it can be seen that for all elements having their strongest lines of the second spectra in the spectral region between 2 200 and 4 600 Å, the Raies Ultimes in this technique always are lines of the second spectra, except Ag and Pd. This exception may be explained by the very high excitation potentials of the strongest lines (Ag II 2246.41 21.9 Volts, Pd II 2296.53 19.8 Volts). The Raies Ultimes

Table 2. The strongest lines of Pb, Pt, Mo and V by the PCE-technique.

Ele-ment	Line *			Sensitivity ppm	Intensity *	
	λ	Classi-fication	Total Excitation Potential		Arc	Spark
Pb	2833 · 069	I	4.4	4	500R	80R
	4057 · 820	I	4.4	4	2 000R	300R
	2203 · 505	II	14.7	10	50	5 000R
	2614 · 178	I	4.7	10	200R	80
	3639 · 580	I	4.4	10	300	50
Pt	2659 · 454	I	4.6	1	2 000R	500R
	2997 · 967	I	4.2	3	1 000R	200
	2929 · 794	I	4.2	10	800R	200
	2830 · 295	I	4.4	10	1 000R	600
	3064 · 712	I	4.0	35	2 000R	300
Mo	2816 · 154	II	11.9	1	200	300
	2848 · 232	II	11.8	3	125	200
	2890 · 994	II	11.7	10	30	50
	2871 · 508	II	11.7	10	100	100
	3902 · 963	I	3.2	10	1 000R	500R
V	2924 · 025	II		0.3	70R	300R
	3033 · 822	II		0.3	20	90R
	2924 · 644	II		1	60	200R
	3267 · 702	II		1	30	80R
	3271 · 125	II		1	25	50R
	3276 · 124	II		1	50	200R
	3093 · 108	II	11.2	1	100R	400R
	3102 · 299	II	11.1	1	70	300R
	3183 · 406	I	3.9	10	200R	100R
	3183 · 982	I	3.9	10	500R	400R
	3185 · 396	I	3.9	10	500R	400R

* Harrison [15].

of all other elements are lines of the first spectra. Two elements, Be and Cd, have equally sensitive lines both of the first and of the second spectra.

The relative intensity order of lines in many cases differs from the data given in wavelength tables. The elements having a line of the first spectrum as Raie Ultime are more regular, *i. e.* the intensity order is mostly equal to data given by Harrison [15] for arc excitation. Lead and platinum, however, show exceptionally great differences, as may be seen in Table II. The elements,

the strongest lines of which arise from singly ionized atoms are very irregular
in this respect. The intensities in general follow the spark excitation data
in wavelength tables, but many deviations were observed. As examples.
the values of molybdenum and vanadium are given in Table II.

All these phenomena find their explanation in the special excitation
technique. When the excitation conditions are altered, great changes in the
appearance of spark and spectra will be observed. When the conditions are
made more arclike by increasing the inductance, the pink colour of the spark,
due according to Feldman (*l. c.*) to the H_α-line, almost disappears and the
sparking tone becomes weaker. The spectrum lacks many bands and lines
caused by carbon or air, and the background effect is weakened. On the other
side, the sensitivity, especially of elements, the Raies Ultimes of which belong
to the second spectra, is largely decreased. It is probable that the differences
observed in different investigations are caused by different excitation con-
ditions.

The strongest lines are necessarily not the best working lines, as is well
known, not even in small concentrations. They may be interfered by lines
of other elements, and this is very important to keep in mind when using
spectrograph with relatively small dispersion. For instance, the three strongest
lines of phosphorus are seldom useful, because iron and manganese interfere.
The best lines of chromium are interfered, too. Because, as has been pointed
out, the relative intensities of lines in this method are often different from
the table values, it is always necessary to determine possible interferences
experimentally. In this work, spectra were taken in all doubtfull cases of
pure solutions of one element.

The application of this method to quantitative analysis of trace elements
in nature waters will be presented in a furthcoming paper.

SUMMARY

The sensitivity limits of the Porous Cup Electrode technique by Feldman
in spectral analysis of solutions were investigated using condensed spark
excitation. The following sensitivities were obtained: 0.02 - 0.1 ppm Ag, Be,
Mn; 0.1—1 ppm Al, Ba, Bi, Cd, Co, Cr, Cu, Fe, Mo, Pt, Sr, V, Zr; 1—10 ppm
As, Ce, Ga, Hg, La, Li, Ni, P, Pb, Sb, Sn, Te, Tl, W, Zn; 10—30 ppm Au,
Na, Th. It has been stated that the most sparklike excitation conditions
produce the greatest sensitivity and that the relative intensities of lines are
often different from those of wavelength tables. The PCE-technique was

found to be the best one in regard to detecting the most elements, only alkalies may be better determined by the flame excitation.

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