

## Spectrochemical Determination of Small Amounts of Calcium in Sodium Chloride

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Method for spectrochemical determination of calcium in sodium chloride in the concentration range of 0.001 to 0.1 % mol.  $\text{CaCl}_2$  with the aid of the line Na 2853 and of one standard is presented. The analytical curve is linear with the slope of  $45^\circ$  in the concentration range under 0.1 % mol.  $\text{CaCl}_2$ ; owing to this, it is possible to work with one standard only.

It is important to determine small amounts of calcium in the single crystals of sodium chloride since these admixtures influence the physical properties of the above crystals. In this case the spectral analysis has certain advantages: high detection limit, velocity, small sample sizes necessary for analysis, etc. Lower precision of this determination is a certain disadvantage but it will be sufficient in most cases.

For quantitative spectrochemical analysis the homologous internal reference line of the matrix element is often used. This line should be in the vicinity of the line of the analysis element and it should have an approximately equal excitation potential [1]. Neither Na nor Cl have available lines near the most suitable Ca lines (I 4226.73 Å — 2.93 eV; II 3933.67 Å — 3.15 eV). For this reason we thought about taking the Na I 2853.03 Å line (doublet 4.35 eV) [2]. Differences in the wave lengths are considerable. Since the slope and the reaction of the spectral plate are different in these two areas (Fig. 1), the line intensities have to be determined from the two calibration curves. For this purpose we used one sample with known Ca content and we recorded its spectrum on each plate together with that of the sample. Thus, measuring the intensity  $I_x$  of the spectral line of the analysis element in rela-

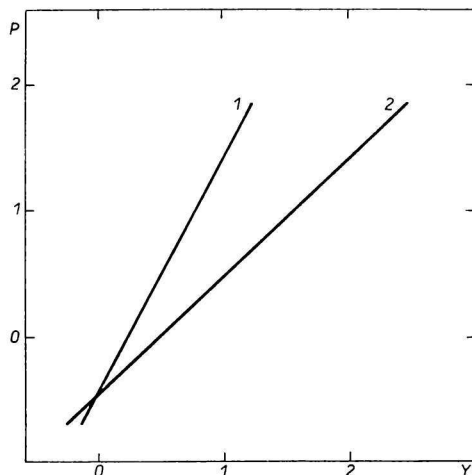


Fig. 1. Calibration curves for the line Ca 4226.73 Å (1) and Na 2853.03 Å (2).

tion to the intensity  $I_r$  of the reference element ( $I_x/I_r$ ), the unknown concentration may be determined.

When we take sufficiently low Ca concentration then at constant conditions of the experiment the number of the emitting Ca atoms will be directly proportional to their concentration. Since the concentration of the Na atoms practically does not change, we can write:

$$\frac{I_x}{I_r} = k [X]. \quad (1)$$

The constant  $k$  may be determined with the aid of the standard with known concentration so that the concentration which is to be determined will be:

$$[X] = \frac{I_x}{I_x^*} \cdot \frac{I_r^*}{I_r} \cdot [X^*], \quad (2)$$

where  $I_x$  = the intensity of the Ca line in the sample,  
 $I_x^*$  = the intensity of the Ca Line in the standard,  
 $I_r^*$  = the intensity of the Na line in the standard,  
 $I_r$  = the intensity of the Na line in the sample,  
 $X$  = the unknown concentration of Ca,  
 $X^*$  = the concentration of Ca in the standard.

At higher concentrations, owing to the influence of different agents (self absorption etc.), this proportionality will be no more valid [3].

We performed several measurements so as to find out how far this method may be used in praxis.

## Experimental

### *Preparation of standard samples*

Standard samples containing 0.5, 0.15, 0.7, 0.05, 0.03, 0.015, 0.01, 0.005, 0.003 % mol.  $\text{CaCl}_2$  were prepared; from among these two were single crystals (0.5 and 0.03 % mol.  $\text{CaCl}_2$ ) and the remaining standard samples were fast-set melts prepared from the aforementioned single crystals to which calculated amounts of NaCl (spectrally pure NaCl by Analar) were added. These mixtures were then put into platinum crucibles, melted in an electric furnace and homogenized. Then the melt was poured into an other platinum crucible and was allowed to set. The samples were prepared either by grinding a part of the melt in an agate mortar or by splintering off a single crystal. The powder was put into the electrodes so as to fill them up to the margin; the single crystal was allowed to protrude 1 mm over the electrode rim.

The standard samples containing 0.5 % mol. and 0.03 % mol.  $\text{CaCl}_2$  were used as single crystals so as to ensure microhomogeneity (especially in repeated runs) and in order to lessen the danger of contamination at handling and storing the standard samples. The distribution coefficient for  $\text{CaCl}_2$  crystal growth from melts is equal to 1 at small concentrations and hence it is possible to assume uniform Ca concentration in the crystal (only 1/3 of the melt crystallized) [4]. Inaccuracies in concentrations which arise by growing the  $\text{CaCl}_2$  crystals in the melt are but relative, as the other standard samples are prepared from these single crystals by adding calculated amounts of NaCl to them.

*Experimental conditions*

Spectrograph: Q 24 Zeiss, Jena.

Electrodes: SU 204/SU 317, Kablo, Topolčany.

Excitation conditions: arc source ABR-3, arc 30 pulses/min, (burning 1/2 sec, intermittence 3/2 sec), current intensity 9 A.

Electrode gap: 1.5 mm.

Intermediate stop: 2 mm.

Slit width: 7.5  $\mu\text{m}$ .

$F$ -number: 11.

Exposure time: 1.5 min.

Photographic material: ORWO Spectral Platten, Blau Hart, WU-2.

Developer: Rodinal 1 20, development time 6 min. at 20 °C.

The following spectra are recorded on a photographic plate:

1. Fe through a 6-step filter (conditions as above, except for the current intensity — 7 A and for the exposure time — 20 sec);
2. the standard sample through a three-step filter;
3. the sample containing over 0.01 % mol.  $\text{CaCl}_2$  through a three-step filter.

Photometer: Schnellfotometer Zeiss, scale P.

From the calibration curves constructed for the lines Ca 4226 and Na 2853 the pertinent  $\log I_x$  and  $\log I_r$  for the standard sample and for the sample may be determined. The calcium concentration in the sample may be calculated from the equation (2).

In cases when there are larger amounts of impurities ( $\text{NaOH}$ ,  $\text{Na}_2\text{CO}_3$ ) in the sample, then the accuracy of the determination is lowered and it is necessary to take a convenient standard sample which would contain impurities similar to those in the analysed sample. Magnesium (the line Mg 2852.13 Å) interferes with the determination.

**Results and discussion**

In Tab. 1 the values  $I_{\text{Ca}}/I_{\text{Na}}$  for both single crystals containing 0.5 and 0.03 % mol.  $\text{CaCl}_2$  are tabulated. Differences in concentration alongside the crystal are within the precision limits of the measurement but in spite of this, when standard samples with lower  $\text{CaCl}_2$  contents were prepared, these were taken from the middle part of the crystal.

Table 1

Ratio  $I_{\text{Ca}}/I_{\text{Na}}$  alongside the crystals grown as standard samples

$I_{\text{Ca } 4226}/I_{\text{Na } 2853}$		
Single crystal NaCl	0.5 % mol. $\text{CaCl}_2$	0.05 % mol. $\text{CaCl}_2$
beginning	10.15	2.81
middle part	11.17	2.68
end	12.85	2.93

*Influence of the excitation conditions*

Since the excitation potentials for Ca and Na are not equal, it is vital to maintain constant excitation conditions, especially the current density. The dependence of the ratio  $I_{Ca}/I_{Na}$  for NaCl with 0.05 % mol.  $CaCl_2$  on the current intensity at constant excitation conditions is shown in Fig. 2. In praxis the current density fluctuations may be kept within the range of  $\pm 5-10\%$ . Changes of the intermediate stop (from 0.8 to 3.2 mm) and changes in the exposure time (1.25–1.75 min) influenced but slightly the value of  $I_{Ca}/I_{Na}$ , in the first case the variations made 7 %, in the latter 12 %.

Table 2  
Dispersion of the values  $\log I_{Ca}/I_{Na}$  at equal exposure conditions

Sample Number	$\log \frac{I_{Ca\ 4226}}{I_{Na\ 2853}}$	Deviation from the mean value %	$\log \frac{I_{Ca\ 3933}}{I_{Na\ 2853}}$	Deviation from the mean value %
1	0.56	-3.8	0.56	-15.7
2	0.62	+6.5	0.74	+11.5
3	0.61	+4.8	0.62	-6.6
4	0.61	+4.8	0.68	+2.4
5	0.61	+4.8	0.68	+2.4
6	0.57	-2.1	0.66	-0.6
7	0.58	-0.35	0.67	+1.0
8	0.54	-7.2	0.70	+5.4
9	0.54	-7.2	0.66	-0.6
Mean	0.582	$s_r = \pm 6\%$	0.664	$s_r = \pm 7.6\%$

From the above data it may be concluded that in the general praxis it will be possible to keep the excitation conditions constant so that the measurement results would be precise to  $\pm 10-15\%$ . Dispersion of the values  $I_{Ca}/I_{Na}$  for nine samples containing 0.05 % mol.  $CaCl_2$  exposed at identical conditions is shown in Tab. 2. As we see, the line for calcium at 4226.73 Å is most suitable for quantitative spectral analysis.

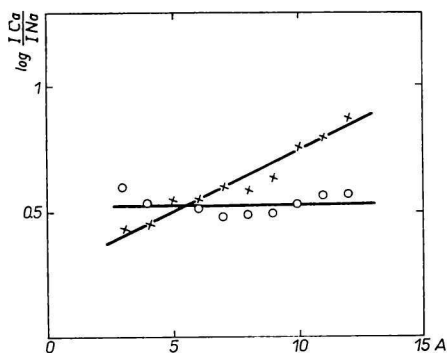


Fig. 2. Dependence of the  $\log I_{Ca}/I_{Na}$  on the change of current intensity for the line Ca 4226.73 Å (○) and Ca 3933.67 Å (×).

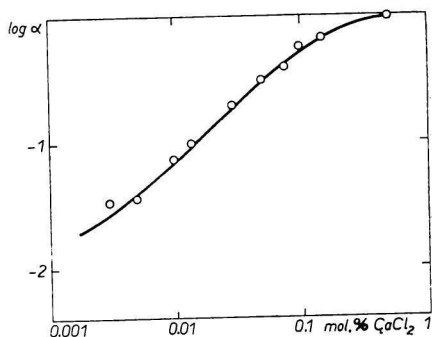


Fig. 3. Uncorrected analytical curve for concentration determination of  $CaCl_2$  in NaCl.

Supposing that all conditions were fulfilled, the standard deviation of the determination is  $\pm 6\%$  of the measured value.

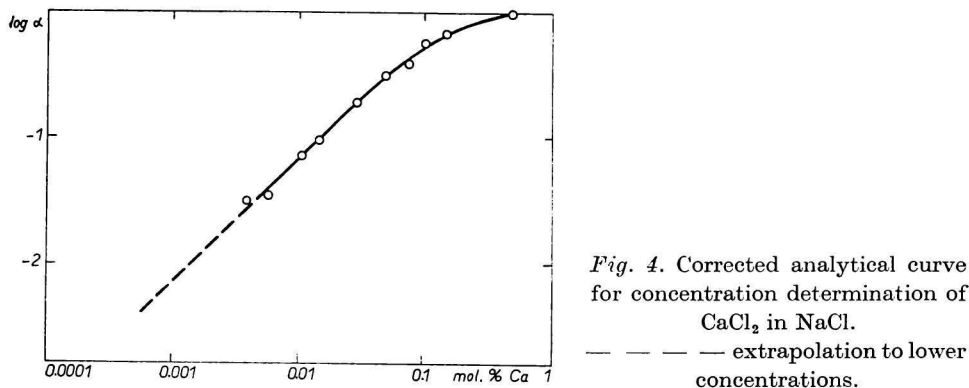
### Construction of the analytical curve

The standard samples were exposed at constant excitation conditions. In the Fig. 3 the dependence of the logarithm of the coefficient  $\alpha$  on the logarithm of the concentration of  $\text{CaCl}_2$  is plotted, where

$$\alpha = \frac{I_{\text{Ca}}}{I_{\text{Ca}}^*} \cdot \frac{I_{\text{Na}}^*}{I_{\text{Na}}} \quad (3)$$

Designation of the intensities is identical with that in the equation (2).

The lower part of the curve diverges slightly from the straight part owing to the influence of the background and to the  $\text{CaCl}_2$  contained in the salt Analar. By extrapolation it was found that the concentration of  $\text{CaCl}_2$  in the salt Analar makes  $0.001\%$  mol. The analytical curve corrected by this value is shown in Fig. 4. The dashed line indicates the prolongation of the straight part of the curve. As it may be seen, the straight part of the curve has a slope of  $45^\circ$ .



### Possibility of extrapolation to lower concentrations

In order to justify the extrapolations to lower concentrations (up to  $0.001\%$  mol.  $\text{CaCl}_2$ ) we performed the measurements with the aid of the radioisotope  $^{45}\text{Ca}$  in the form of a chloride with activity  $0.05$  mCi/ml.

We added small amount of the radioisotope  $^{45}\text{Ca}$  to the  $10\%$  solution of  $\text{NaCl}$  (Analar). A part of this solution was incompletely extracted with 8-hydroquinoline in chloroform [5–7]. By this procedure we got, apart from the initial solution, a partly extracted solution of  $\text{NaCl}$ . From each of these solutions we pipetted  $10$  ml and we allowed every sample to evaporate separately on a quartz dish. After complete evaporation to dryness, the  $\text{Ca}$  concentration was determined spectrochemically with the aid of an extrapolated analytical curve. For this determination standard samples containing  $0.05$  and  $0.01\%$  mol.  $\text{CaCl}_2$  were used. By the extraction of  $10$  ml of the initial solution and of  $10$  ml of partly extracted solution we obtained two

portions of the organic phase which we evaporated to dryness and measured their activities. The results of these measurements are shown in Tab. 3.

The ratio of the concentrations of  $\text{CaCl}_2$  in the initial and in the partly extracted solution of  $\text{NaCl}$  is 5.6, the ratio of the activities in these solutions is 4.7. With regard to low concentrations and to difficulties in determinations of the activities of the radioisotope  $^{45}\text{Ca}$ , we consider the above agreement of ratios as satisfactory and in our opinion it justifies the extrapolation of the analytical curve to lower concentrations.

Table 3  
Verification of the extrapolation of the analytical curve

Sample	Concentration $\text{CaCl}_2$ determined by spectrochemical analysis (% mol.)	Activity of the samples (imp/min)
Standard sample with 0.05 % mol. $\text{CaCl}_2$	0.05	—
Standard sample with 0.01 % mol. $\text{CaCl}_2$	0.0108	—
Non-extracted sample	0.0058	690
Partly extracted sample	0.00104	146

Theoretically, this extrapolation should be possible to infinity, practically there are several limitations, first as regards the detection limits, which among others, depend on the quality of the photographic paper, then on the calcium contamination of the spectral carbon electrodes. We made the experience that the line  $\text{Ca } 4226$  may be still well measured at concentrations of 0.001 % mol.  $\text{CaCl}_2$  but the estimations may be made as far as 0.0001 % mol.  $\text{CaCl}_2$ . Higher detection limit may be achieved by extraction enrichment with 8-hydroquinoline. We did not study in details this special problem.

## SPEKTROCHEMICKÉ STANOVENIE MALÝCH MNOŽSTIEV VÁPNIKA V CHLORIDE SODNOM

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Vypracovala sa metóda na stanovenie malých množstiev  $\text{CaCl}_2$  v monokryštáloch  $\text{NaCl}$  v rozmedzí koncentrácií 0,001—0,1 % mol.  $\text{CaCl}_2$ . Pri stanovení založenom na metóde jedného štandardu sa použila čiara  $\text{Na } 2853,03 \text{ \AA}$  ako čiara vnútorného štandardu a čiara stanovovaného prvku  $\text{Ca } 4226,73 \text{ \AA}$ . Analytická krivka získaná pomocou niekoľkých štandardov je pod koncentráciou 0,1 % mol.  $\text{CaCl}_2$  lineárna so sklonom  $45^\circ$ . Štandardná odchýlka stanovenia je  $\pm 6 \%$ .

Opisuje sa aj príprava štandardných vzoriek a uvádza sa overenie možnosti extrapolácie analytickej krivky do nižších koncentrácií.

СПЕКТРОХИМИЧЕСКОЕ ОПРЕДЕЛЕНИЕ МАЛЫХ КОЛИЧЕСТВ КАЛЬЦИЯ  
В ХЛОРИДЕ НАТРИЯ

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Был разработан метод для определения малых количеств  $\text{CaCl}_2$  в монокристаллах  $\text{NaCl}$  в интервале концентраций 0,001—0,1 % *мол.*  $\text{CaCl}_2$ . Определение основано на методе одного стандарта. Для определения использовали линию  $\text{Na}$  2853,03 Å как линию внутреннего стандарта, а также линию определяемого элемента  $\text{Ca}$  4226,73 Å. Аналитическая кривая, полученная с помощью нескольких стандартов, при концентрациях меньше, чем 0,1 % *мол.*  $\text{CaCl}_2$  линейна с наклоном 45°. Стандартное отклонение определения  $\pm 6\%$ .

В работе также описывается приготовление стандартных образцов и проверка возможности экстраполяции аналитической кривой к более низким концентрациям.

Перевела Т. Диллингерова

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