

EXTRACTION-CHROMATOGRAPHIC SEPARATION OF BORON ON A COLUMN WITH STATIONARY SOLUTION OF 2,3-NAPHTHALENEDIOL AND DIPHENYLGUANIDINE

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Received May 16th, 1975

A new method has been developed for the separation of boron from interfering anions (F^- and NO_3^-) for its photometric determination with quinalizarine. Boron (in the form of boric acid) is held on a column packed with teflon impregnated with a solution of 2,3-naphthalenediol and diphenylguanidine in isoamyl alcohol. With the aqueous phase fluorides and nitrates and, in addition, phosphates and chlorides are washed out, and boron is eluted with 0.1M sulfuric acid. The separation was successful even with a 50-fold excess of nitrates and a 20-fold excess of fluorides. The error for the separation of 20–50 μg of boron was 2 to 7%.

For a photometric separation of boric acid, boron must be usually separated from interfering anions. During experimental tests of the various methods of determination of small amounts of boric acid, particularly in plant materials (photometric determination with curcumine, quercetin carminic acid, and quinalizarine, fluorimetric determination with benzoin), the quinalizarine method proved to be the most suitable. With this method of determination, however, the presence of fluoride and nitrate ions interferes¹. For an analytical separation of small amounts of inorganic components, their extraction proved to be of advantage. If, however, such a system, where the recovery is quantitative, is not known, and if none of the properties of the extract can be employed for the determination of the component separated, it is more convenient for quantitative analysis to apply extraction chromatography (reversed phase partition chromatography) than a multiple extraction and successive reextraction of the component determined from the combined extracts into the aqueous phase.

In our previous works we selected solution of 2,3-naphthalenediol (ND) and diphenylguanidine (DPG) in n-butanol as the best system for the isolation of boric acid², and examined the effect of the various factors on the recovery³. We found that with the organic phase obtained by dissolving $5 \cdot 10^{-2} \text{ mol.l}^{-1}$ of ND and $5 \cdot 10^{-2} \text{ mol.l}^{-1}$ of DPG in n-butanol, 97% of boron can be extracted (for $V_{\text{org}} = V_{\text{aq}}$).

In this work we sought conditions of extraction-chromatographic separation of boric acid from aqueous solutions such to remove anions interfering with photometric determination of boron with quinalizarine. The commonly used separation by distillation of boric acid methyl ester is time consuming and inconvenient from analytical point of view.

EXPERIMENTAL

Chemicals and Apparatus

2,3-Naphthalenediol 99% (Schuchardt), diphenylguanidine *p.a.* (Fluka), and boric acid *p.a.* (Lachema, Brno) were used. Boric acid was purified by crystallization, isoamyl alcohol by double distillation. All the other chemicals were *p.a.* purity.

Teflon (Becker, Delft, The Netherlands), Teflex (poly(trifluorochloroethylene)) (Spolek pro chemickou a hutní výrobu, Ústí nad Labem), Synachrom E5 (styrene-divinylbenzene copolymer) (Lachema, Brno), and silica gel (Merck, Darmstadt, FRG) were used as the supports. The latter was dried for 2 h at 105–110°C and hydrophobized by shaking with dimethyldichlorosilane (1 : 1 wt/wt) and heating up to 110°C (see⁴). The supports were sieved in the dry state. Their specific surface area was determined by using the method of thermal desorption of nitrogen.

For the pH measurements a compensation pH-meter PHK 1 (Mikrotechna, Prague) with a glass electrode SEV 2 and a saturated calomel electrode KALC (Laboratorní přístroje, Prague) was employed. The measuring cell was calibrated by means of a set of standard buffers of NBS. The photometric measurements were performed on instruments Spekol (Zeiss, Jena, GDR) and SF4 (USSR).

The content of boron in an eluate was determined photometrically with quinalizarine¹, fluorides and nitrates were determined also photometrically, with zirconalizarine and with phenoldisulfonic acid, respectively⁵.

Chromatographic Columns and Working Procedure

The chromatographic columns (7 × 110 mm) were equipped with a tap for the control of the flow rate. Over the tap a low layer of glass wool, which had been boiled with hydrochloric acid, was rammed. The dry support was introduced with mild tapping. The top of the column was plugged with glass wool. The stationary organic phase was obtained by shaking the extractant with the aqueous solution. Their volume ratios and compositions are always given. The organic phase was sucked in from a weighed amount in a weighing bottle by means of a pump; this ensured at the same time the removal of air bubbles from the column. The organic phase was added

TABLE I

Dependence of Boron Extraction Recovery on the Concentration of 2,3-Naphthalenediol and Diphenylguanidine in Isoamyl Alcohol

$$c_B = 3.41 \cdot 10^{-3} \text{ mol.l}^{-1}, I 0.2, \text{pH } 2.24, V_{\text{aq}} = V_{\text{org}}$$

$c_{\text{DPG,org}}$ mol.l ⁻¹ · 10 ⁻²	$c_{\text{DN,org}}$ mol.l ⁻¹ · 10 ⁻²	<i>E</i> %	<i>D</i>
5.0	5.0	96.0	23.7
5.0	2.5	94.7	17.6
5.0	1.25	90.2	9.2
5.0	0.5	80.8	4.2
2.5	5.0	95.2	19.6
1.25	5.0	88.5	7.7

in an amount to reach the top of the support column. The volume of the liquid transferred (V_t) was found by weighing the weighing bottle. The column was washed with the corresponding aqueous phase until the free organic phase, whose volume equals that of the mobile phase, V_m , was completely removed. The volume of the stationary phase was calculated from the difference, $V_s = V_t - V_m$.

The sorption capacity of the supports used was determined as follows: A weighed amount of the support was brought in contact with the organic phase in a weighing bottle, the mixture was shaken and allowed to stand for 2 h. The impregnated support was then separated from the nonadsorbed organic phase by filtration with a weighed glass crucible, whose filtration disc had been before saturated with the organic phase. The volume of the organic phase held was calculated from the weight increase. The data so obtained (statistically evaluated) are in a good agreement with the analogous data found in the column (by the dynamic method) (Table II).

The ionic strength of the aqueous (mobile) phase was always 0.2 (Na_2SO_4) and the pH was adjusted by using 1M- H_2SO_4 (see³).

RESULTS AND DISCUSSION

As the solvent constituting along with ND and DPG the stationary phase, isoamyl alcohol was chosen; its solubility in water is lower than that of n-butyl alcohol, which has been used for the study of static extraction of the system in question. Although the solvents have very similar properties, we compared the extraction recoveries obtained with isoamyl alcohol with the results obtained previously with n-butanol³. The dependence of the percentage extraction of boron on the concentrations of ND and DPG in isoamyl alcohol is given in Table I. The differences found (e.g., $E = 96.7\%$ with n-butyl alcohol and 96% with isoamyl alcohol, with the concentrations of ND and DPG $5.0 \cdot 10^{-2} \text{ mol l}^{-1}$ in both cases) are insignificant.

The supports used were mutually compared with respect to the amount of sorbed organic phase per mass unit and with respect to their specific surface area. The sorption was carried out both dynamically and statically. The organic phase, from which the sorption proceeded, was obtained as follows: Solution containing $5 \cdot 10^{-2} \text{ mol.l}^{-1}$ of ND and the same concentration of DPG in the corresponding solvent was shaken with an equal volume of the aqueous phase (pH 2.30, I 0.2), and the organic phase was then separated.

Among the supports tested, Synachrom has the largest specific surface area and sorbs the highest volume of the organic phase per mass unit. This is apparent from Table II listing the data obtained for various grain size of the supports and for sorption from solvents, which also gave good results during the selection of the extraction system². Synachrom in contact with water swells so, that the flow rate of the mobile phase in the column is too low (1–2 drops per minute), if no flow pump is applied. PVC, Teflon, and Teflex have very similar sorption capacities for the stationary liquid phase used, which is in accordance with their specific surface areas⁶. For PVC in the column only very low flow rates were attained when no flow pump was applied; this was due to the small grain size of this support.

Silica gel has a considerably larger specific surface area than the organic supports used (except for Synachrom), but its sorption capacity is almost the same as that of PVC, Teflon, or Teflex. As found⁷, specific surface area of polar supports drops to 10% of the initial value or less, in dependence on their hydrophobization procedure. The sorbed amount of the organic phase is, however, lower than expected even when this lowered specific surface area is taken into account. This can be explained by an incomplete hydrophobization of the surface and so an imperfect removal of the polar character of the support.

We tested also the effect of the type of solvent on the sorption of the organic phase on the support. If this sorbed amount is expressed as the volume per mass unit, which is more appropriate from the aspects treated, there is no significant difference between isoamyl alcohol and nitrobenzene. From solutions in 1,2-dichloroethane the sorption is lower. Nitrobenzene was not applied, with regard to its higher toxicity. Teflon impregnated with the organic phase obtained from a solution of ND and DPG in isoamyl alcohol was therefore used as the stationary phase.

TABLE II
Sorption of the Organic Phase on Supports

Support	d_p mm	Specific surface area $m^2 g^{-1}$	Amount sorbed		
			batch-wise		dynamically
			g/g	ml/g	ml/g
PVC ^a	0.05	—	0.46	0.57	—
PVC ^a	0.05—0.12	—	0.51	0.63	0.59
Synachrom ^a	0.12—0.16	—	1.81	2.20	—
Synachrom ^a	0.16—0.20	373	1.88	2.29	2.24
Synachrom ^b	0.16—0.20	373	2.61	2.17	—
Teflex ^a	0.05—0.12	—	0.49	0.60	—
Teflex ^a	0.12—0.25	—	0.49	0.60	—
Teflex ^a	0.25—0.50	3.44	0.55	0.66	0.60
Teflex ^b	0.25—0.50	3.44	0.70	0.58	—
Teflon ^a	0.12—0.25	—	0.42	0.52	—
Teflon ^a	0.25—0.50	2.22	0.40	0.48	0.54
Teflon ^b	0.25—0.50	2.22	0.60	0.50	—
Teflon ^c	0.25—0.50	2.22	0.23	0.18	—
Silica gel ^a	0.05—0.12	—	0.44	0.54	—
Silica gel ^a	0.12—0.25	272 ^d	0.44	0.54	0.56

^{a-c} Solvent used for the preparation of the organic phase: ^a isoamyl alcohol, ^b nitrobenzene, ^c 1,2-dichloroethane. ^d Specific surface area determined prior to hydrophobization.

The suitability of this system was confirmed also by the sorption and elution of boron on a column packed with 2 g of Teflon, Teflex, or hydrophobized silica gel, impregnated with the stationary liquid phase ($5 \cdot 10^{-2}\text{M-ND}$, + $5 \cdot 10^{-2}\text{M-DPG}$ after shaking with an equal volume of the aqueous phase, pH 2.30) by the dynamic procedure. 200 μl of an aqueous solution of boric acid containing 18.4 μg of boron was brought on the column (L 72 mm, $d_p = 0.12-0.25$ mm, V_s 1.2 ml, V_m 1.3 ml). The column was washed with the aqueous phase ($F_m = 0.15-0.20$ ml min^{-1}) and the content of boron was determined in the aliquots of the eluate. With Teflex or Teflon as the support, boron was not detected in the eluate even after the elution with 110 or 270 ml of the aqueous phase; with silica gel boron passes into the first fractions of the eluate. However, only 70% of the boron present were eluted, the remaining amount can be eluted with 0.1M sulfuric acid.

In order to prove that the distribution of boron between the mobile and stationary phases is governed by the Nernst distribution law, we followed the dependence of the elution volume of boron on the concentration of ND in the stationary phase at a constant pH value and ionic strength in the mobile phase and constant concentration of DPG in the stationary phase. The value of the elution volume is given by the relation $V_R = V_m + DV_s$ and, as proved in the previous work³, D depends on the

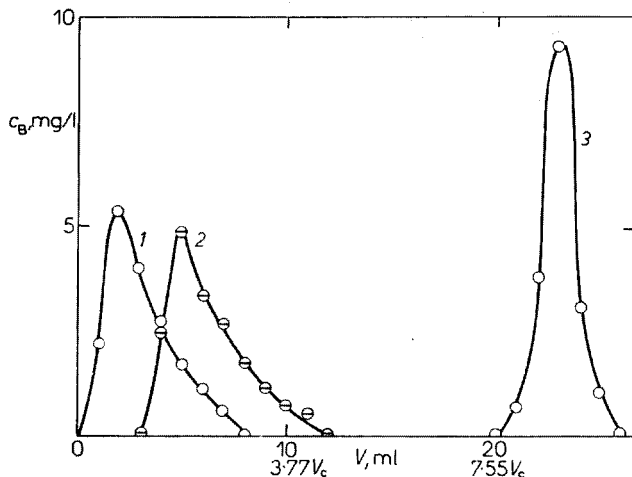


FIG. 1

Dependence of the Elution Volume of Boron on the Concentration of 2,3-Naphthalenediol in the Stationary Phase

Column 7×110 mm, V_c 2.67 ml; mobile phase: pH 2.30, I 0.2; stationary phase: Teflon, $d_p = 0.25-0.50$ mm, impregnated with the organic phase obtained by equilibration of $5.0 \cdot 10^{-2}\text{M-DPG}$ and $1.50 \cdot 10^{-3}$, $2.125 \cdot 10^{-2}$, $3.25 \cdot 10^{-2}\text{M-ND}$ in isoamyl alcohol with the mobile phase ($V_{org} : V_{aq} = 1$). Introduced 18.4 μg B (as H_3BO_3) in 200 μl .

concentration of ND in the organic phase during static extraction. From Fig. 1 it is clear that V_R depends on the concentration of ND in the stationary phase, hence the distribution obeying the Nernst law is the predominant process.

From the relation for V_R we calculated the value D_{chrom} and compared it with the value D_{ex} for static extraction under identical conditions:

$c_{\text{ND,org}}(\text{M})$:	$2.5 \cdot 10^{-2}$	$1.25 \cdot 10^{-2}$	$5.0 \cdot 10^{-3}$
D_{chrom} :	20.0	3.98	0.46
D_{ex} :	17.6	9.2	4.2

Some agreement of the two values can be found only for $c_{\text{ND,org}} = 2.5 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}$. With decreasing concentration of ND the difference of the two values increases. On the other hand, when the concentration of ND was raised up to $5.0 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}$, a value $V_R > 270 \text{ ml}$ was found, hence $D_{\text{chrom}} > 240$, which is much higher than as extraction ($D_{\text{ex}} = 24$). The explanation of those differences is aggravated by the fact that the volume of the sample introduced amounts to approx. 15% of V_m : as a matter of fact, the concentrations of the active components in the stationary phase change, as all the three components (particularly DPG) dissolve partly in water; this concentration changes manifest themselves more when low concentrations of the extractant are applied.

The V_R value depends not only on the concentration of ND, but analogously also on that of DPG. The concentrations of these two components in the stationary phase vary with the ratio of the volumes of the organic and aqueous phases during their equilibration before the impregnation of the support: the concentrations decrease with increasing ratio $V_{\text{aq}}:V_{\text{org}}$, which showed up in the decreasing V_R value.

For the examination of this dependence a solution containing $5.0 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}$ of ND and $5.0 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}$ of DPG in isoamyl alcohol, which had been equilibrated with an aqueous solution of pH 2.30 and I 0.2 in the ratios $V_{\text{aq}}:V_{\text{org}} = 1, 2, 3, 4, \text{ and } 5$, respectively, was used. On the column packed with Teflon ($d_p = 0.25$ to 0.5 mm), $18.45 \mu\text{g}$ of boron in $200 \mu\text{l}$ of a boric acid solution was introduced and the elution was carried out with the aqueous phase from the equilibration. The volume of the eluate containing boron in particular cases is apparent from the following table:

$V_{\text{aq}}/V_{\text{org}}$:	1	2	3	4	5
V (multiple of V_c):	>100	>11	0-3.2	0-1.7	0-1.7
%B eluted from the column:	0	0	54	100	100

The residue of boron remaining in the column after the elution with the aqueous phase could be removed by washing with $0.1\text{M-H}_2\text{SO}_4$.

So if the ratio of the volumes of the organic and aqueous phase used during the preparation of the solution for the impregnation of the support is ≥ 3 , boron passes the column with the front of the mobile phase. For a perfect retention of boron this ratio must be < 2 . The volume of the sample solution introduced must be as small as possible, with regard not only to the broadening of the peaks, but also to the decrease of the concentrations of the active components in the stationary phase as mentioned above.

Further we sought the amount of $0.1\text{M-H}_2\text{SO}_4$ required for washing out the boron held on the column. $200\ \mu\text{l}$ of boric acid solutions of various concentrations were introduced on columns (support: Teflon $0.25-0.50\ \text{mm}$; $L\ 90\ \text{mm}$, $V_c\ 3.40\ \text{ml}$, org: $5.0 \cdot 10^{-2}\ \text{mol.l}^{-1}\ \text{ND} + 5.0 \cdot 10^{-2}\ \text{mol.l}^{-1}\ \text{DPG}$ in isoamyl alcohol; aq: pH 2.3, $I\ 0.2$; $V_{\text{aq}}/V_{\text{org}} = 1$, $F_m = 0.4 - 0.6\ \text{ml min}^{-1}$), the columns were washed out with $10\ \text{ml}$ of the aqueous phase ($\approx 3\ V_c$) and then washed with $0.1\text{M-H}_2\text{SO}_4$. Boron was determined in the eluate portions. The results are given in the following table and are depicted in Fig. 2.

Boron introduced, μg :	9.20	17.20	17.48	24.40
Washed out, μg :	10.0	17.3	17.3	25.5
Volume of $0.1\text{M-H}_2\text{SO}_4$, V_c :	1.1	1.1	1.3	1.6

Obviously boron can be washed out of the column quantitatively in a relatively

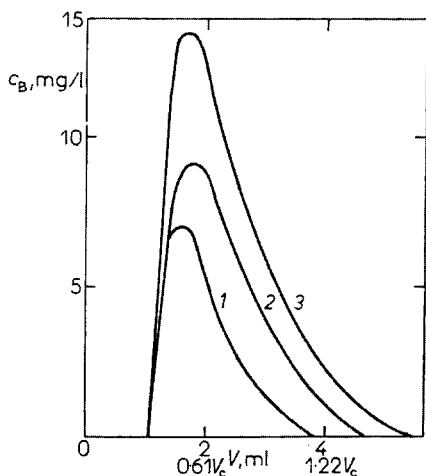


FIG. 2
Elution of Boron with $0.1\text{M-H}_2\text{SO}_4$
 μg of boron introduced: 1 9.20, 2 17.48,
3 24.40. All the conditions given in the text.

narrow fraction ($1.6 V_c = 5.3$ ml). The elution curves exhibit a slight tail, the peak width is due to the rather bulk support grain.

As with most of the photometric methods of determination of boron the presence of fluorides and nitrates interferes, we investigated also chromatographic behaviour of those anions in the chromatographic column described. The two ions were introduced in the form of 200 μ l of an aqueous solution and the eluate portions were analyzed during elution with the aqueous phase. The results showed that the two anions pass the column with the front of the elution solution and 1.5 and 1.8 V_c was sufficient for washing out 180 μ g of F^- and 1 mg of NO_3^- , respectively.

The possibility of separation of boron from nitrates and fluorides was proved by the following test: A mixture of 9.20 μ g of B and 500 μ g of NO_3^- in 200 μ l solution was introduced on the column, the column was washed with 1.5 V_c of the aqueous phase and boron was then eluted with 1.5 V_c of 0.1M- H_2SO_4 . In the eluate 9.40 μ g of boron was found. Similarly, 8.72 μ g of B was eluted from 9.20 μ g introduced together with 179.1 μ g of F^- . The deviations in the boron contents found (+2.2% and -5.2%, respectively) lie within the limits of error of photometric determination of boron.

The accuracy and reproducibility of the chromatographic separation of boric acid by the procedure suggested was tested by the analysis of model samples containing 55.0 mg F^- /l, 51.5 mg PO_4^{3-} /l, 58.0 mg NO_3^- /l, and 49.5 mg Cl^- /l. The concentrations of boron were 4.60, 7.96, and 10.96 mg/l. The separation was performed as follows:

Procedure: 5 ml of the sample is pipetted in a platinum crucible, 0.05 ml of 0.1M- Na_2CO_3 is added (for the boric acid not to volatilize) and the solution is evaporated to dryness at 90°C. The residue is dissolved in a small volume of the aqueous phase (after its equilibration with the organic phase), the solution is transferred on the column and the crucible is washed with additional small portions of the aqueous phase. The column is washed with 10 ml of the aqueous phase and boron is then

TABLE III
Analysis of a Model Sample

Boron introduced, μ g	23.0		39.8		54.8	
V_m , ml	1.60	1.30	1.50	1.40	1.40	1.20
V_s , ml	1.50	1.55	1.50	1.60	1.46	1.60
F_m , ml min ⁻¹	0.45	0.40	0.60	0.50	0.55	0.50
Boron found in the eluate, μ g	24.5	22.5	38.2	37.8	49.8	52.4
\bar{x} , μ g	23.5		38.0		51.1	
Δ , %	+2.2		-4.5		-6.7	
s , μ g			1.4			

eluted with 10 ml of 0.1M-H₂SO₄. The eluate is collected in a 10 ml volumetric flask and the concentration of boron is determined by the quinalizarine method.

Preparation of the column: Teflon (~2.5 g, 0.25–0.50 mm) is impregnated in a column (7 × 100 mm) with the extractant obtained by shaking the organic phase (5.0 · 10⁻²M-ND + 5.0 · 10⁻²M-DPG in isoamyl alcohol) with the aqueous phase (pH 2.30, I 0.2 (Na₂SO₄), V_{aq}/V_{org} = 1). The unadsorbed organic phase is washed out with the aqueous phase obtained after its equilibration with the organic phase.

The results obtained are given in Table III. The estimate of the standard deviation was calculated⁸ from a parallel determinations of all the three concentrations.

LIST OF SYMBOLS

d_p	diameter of the support particles
D	distribution ratio
E	percentage extraction
F_m	volume flow rate of the mobile phase
I	ionic strength
L	length of the column
s	standard deviation
V_{aq}	volume of the aqueous phase
V_c	total volume of the column
V_m	volume of the mobile phase
V_{org}	volume of the organic phase
V_K	elution volume
V_s	volume of the stationary phase
\bar{x}	average value
Δ	error

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Translated by P. Adámek.