

SELECTION OF AN EXTRACTION SYSTEM FOR THE ISOLATION OF BORIC ACID BY REVERSED PHASE PARTITION CHROMATOGRAPHY

F. VLÁČIL and K. DRBAL

*Department of Analytical Chemistry, Institute of Chemical Technology, 166 28 Prague 6 and
Department of Chemistry, Institute of Agriculture, 370 00 České Budějovice*

Received January 16th, 1975

A suitable extraction system was sought for the isolation of boron by reversed phase partition chromatography (RPPC). From several tested chelate forming agents yielding a complex anion with boric acid, and from organic cations forming an extractable ionic associate with this complex anion, the system 2,3-naphthalenediol–diphenylguanidine–butanol was selected; with this system (pH of the aqueous phase ≈ 2), 97% of boron is transferred to the organic phase by a single extraction.

Most of the photometric methods of determination of boric acid require its isolation from interfering ions, *e.g.* fluorides, which form the complex anion BF_4^- with borates, or nitrates, which interfere by their oxidation effect. Distillation of methylester of boric acid, commonly used for isolation, is inconvenient, and for separation of small amount of boron not reliable. Newer methods of isolation are based on ion exchange on anion exchanger^{1,2} or selective ion exchangers³, or extraction. In acidic media, boric acid itself can be extracted with 3-methyl-1-butanol⁴ or tri-*n*-butylphosphate⁵. Very often the extraction of the ionic associate of BF_4^- with a coloured organic cation (*e.g.* methylene blue⁶) is used for analytical purposes. In both of the extraction types low distribution ratios ($D \approx 8$) are attained. The extraction of boric acid at pH 2–8 as complexes with some aliphatic or aromatic diols ($D \approx 20-60$) has been also studied⁷. Bock and Vrchlábský⁸ obtained a 93–98% extraction of boric acid in the presence of pyrocatechol and diphenylguanidine or tetraphenylarsonium bromide.

We attempted to utilize the hitherto published data on extraction of boron to develop a method of its separation by the reversed phase partition chromatography (extraction chromatography). For this purpose, system composed of an aromatic vicinal diol and a suitable organic cation appeared to be most appropriate. Such reagents (H_2L) can form⁹ with boron complexes $\text{BL}(\text{OH})$, $\text{BL}(\text{OH})_2^-$, or BL_2^- . According to other authors¹⁰⁻¹⁵, aromatic vicinal diols form with boric acid at $c_{\text{L}} > c_{\text{B}}$ predominantly complexes $\text{BL}(\text{OH})_2^-$. In this work we aimed at selecting an appropriate extraction system, *i.e.* a chelate forming agent, organic cation, and solvent, suitable for the isolation of boron by extraction chromatography.

EXPERIMENTAL

Chemicals and Apparatus

2,3-Naphthalenediol (99%) and tetraphenylarsonium chloride *p.a.* (Schuchardt, FRG), diphenylguanidine (Fluka, Switzerland), crystal violet (BDH, England) were commercial chemicals; boric acid *p.a.* (Lachema, Brno) was purified by recrystallizing and drying at 110°C. Ferroin and tris(1,1'-dipyridyl)ferrous sulfate were prepared from Mohr's salt and the corresponding reagents so that the concentration of the complex was $2.0 \cdot 10^{-2} \text{ M}$ and the solutions contained a 50% excess of the reagent. The organic solvents used were redistilled twice, the other chemicals (*p.a.*, Lachema) were not further purified.

The pH values were measured by using a compensation pH meter PHK 1 (Mikrotechna, Prague) with a glass electrode SEV 2 and a saturated calomel electrode KALC (Laboratorní přístroje, Prague). The measuring cell was calibrated by means of a set of standard buffers of NBS. Spectrophotometric measurements were performed on an instrument Spekol (Zeiss, Jena) or SF-4 (USSR). The temperature was kept at $20 \pm 1^\circ \text{C}$ during all experiments.

The following photometric methods were tested for the determination of boron: the curcumine, quercetin, and quinalizarine methods, determination with carminic acid, and luminescence determination with benzoin. With respect to the simplicity of the technique, reproducibility, and interfering effects, the quinalizarine¹⁶ method proved to suit best for the determination of boron. It yielded linear working plots up to the concentration 8 mg B/l, the limit of determination¹⁷ $c_{\text{min}} = 0.46 \text{ mg B/l}$.

When organic compounds did not interfere, boron was determined directly in the equilibrium aqueous phase. The blank was represented by the aqueous phase obtained by equilibrating the corresponding aqueous solution without boron with the extractant. In cases that the reagents present or the coloration of the aqueous phase interfered with the determination, the sample was mineralized after mixing with soda by evaporating and annealing¹⁸ at 500–550°C.

RESULTS

Selection of the complexing agent. An aqueous solution of boric acid was adjusted to pH 1.6, 3.4, 6.5, or 11.3 by means of sulfuric acid and sodium hydroxide and extracted with butanol ($V_{\text{org}} = V_{\text{aq}}$) in the presence of $5.0 \cdot 10^{-2} \text{ mol l}^{-1}$ of diphenylguanidine and $5.0 \cdot 10^{-2} \text{ mol l}^{-1}$ of one of the following reagents: pyrocatechol, pyrogallol, tiron, chromotropic acid, salicylic acid, 2,3-naphthalenediol. The solvent and diphenylguanidine were selected according to preliminary experiments. The results obtained (percentage extraction of boron) are given in Table I.

2,3-Naphthalenediol appeared to be the most suitable reagent, not interfering — in contrast to pyrocatechol — with direct photometric determination of boron.

Selection of the organic cation. The effect of the organic cation on the extraction of the complex of boric acid with 2,3-naphthalenediol $[\text{BL}(\text{OH})_2^-]$ had to be followed at various pH values of the aqueous phase. Buffer solutions were not used for adjusting pH, in order to eliminate the effect of formation of complex compounds of their components with boric acid on the extraction equilibria. The pH value and ionic strength were adjusted by means of a strong inorganic acid and sodium hydroxide.

The equilibrium pH value was measured and the effect of the inorganic acid ions present on the percentage extraction of boric acid was followed; the concentration of the acid was determined directly in the aqueous phase in case that diphenylguanidium, tetraphenylarsonium, or octadecylammonium was the organic cation. The results obtained are given in Table II.

During the examination of the effect of the cations $[\text{Fe}(\text{phen})_3]^{2+}$, $[\text{Fe}(\text{dipy})_3]^{2+}$ (phen is *o,o'*-phenanthroline, dipy is 1,1'-dipyridyl), and crystal violet, the influence of the solvent type on the completeness of extraction was studied as well. Since the aqueous phase was coloured, it was mineralized prior to the determination of boron. The results are summarized in Table III.

The use of dichloromethane as the solvent and 2,3-naphthalenediol as the complexing agent, and addition of the dipyridyloferrous or phenanthroline-ferrous cation leads to a virtually complete extraction of boron. A lower recovery is obtained in the presence of crystal violet. In all cases, an excess of the organic cation in the extraction system brings about coloration of the aqueous phase after the extraction.

Selection of the solvent for the extraction system 2,3-naphthalenediol-diphenylguanidine (or tetraphenylarsonium chloride or octadecylamine). For adjusting the optimum pH and ionic strength ($I\ 0.1$), $1\text{M-H}_2\text{SO}_4$, 1M-NaOH , and $1\text{M-Na}_2\text{SO}_4$ were applied. The two phases ($V_{\text{org}} = V_{\text{aq}}$) were shaken for 10 minutes, which was sufficient for the extraction equilibrium to establish.

The extractant for the combination H_2L -diphenylguanidine was obtained by mixing 0.1M solutions of the two components in the vol. ratio 1 : 1. When the solubility of some of the components was lower than $0.1\ \text{mol l}^{-1}$, its saturated solution was prepared. The pH of the aqueous phase, containing $3.21 \cdot 10^{-3}\text{M-H}_3\text{BO}_3$, was ad-

TABLE I

Percentage Extraction (E) of Boron with Butanol in the Presence of Various Complexing Agents and Diphenylguanidine

pH 3.40, $V_{\text{org}} = V_{\text{aq}}$, $c(\text{diphenylguanidine}) = 5.0 \cdot 10^{-2}\ \text{mol l}^{-1}$, $c(\text{reagent}) = 5.0 \cdot 10^{-2}\ \text{mol l}^{-1}$, $c(\text{H}_3\text{BO}_3) = 3.21 \cdot 10^{-3}\ \text{mol l}^{-1}$.

| Complexing agent | $\text{p}K_{\text{a}1}^a$ | $\text{p}K^{a,b,c}$ | $E, \%$ |
|---------------------|---------------------------|---------------------|---------|
| Chromotropic acid | 5.33 | 1.55 | 35.0 |
| Salicylic acid | 3.00 | 1.6 | 50.0 |
| Tiron | 7.64 | 3.74 | 52.0 |
| Pyrogallol | 9.05 | 5.36 | 60.0 |
| Pyrocatechol | 9.40 | 5.18 | 91.0 |
| 2,3-Naphthalenediol | 8.68 | 4.10 | 93.0 |

^a see 10^{-12} ; ^b $K(\text{H}_3\text{BO}_3 + \text{H}_2\text{L} \rightleftharpoons \text{BL}(\text{OH})_2^- + \text{H}^+ + \text{H}_2\text{O})$; ^c with $c_{\text{L}} > c_{\text{B}}$.

justed to 2.12. For the combination H_2L -tetraphenylarsonium chloride, 0.1M- H_2L in the corresponding solvent (or the saturated solution) served as the extractant, the aqueous phase (pH 11.20) contained boric acid and tetraphenylarsonium chloride in concentrations $1.70 \cdot 10^{-3}$ and $5.0 \cdot 10^{-2}$ mol l $^{-1}$, respectively. For the extraction with the system H_2L -octadecylamine, the solution of the amine was prepared as follows: a weighed portion of octadecylammonium chloride was mixed with a small excess of 2M-NaOH and extracted with 20 ml of the solvent to yield the organic phase, which was washed several times with water saturated with the solvent and octadecylamine until it gave an almost neutral reaction, and then made to the mark of a volumetric flask. The amine concentration was then found by determining the content of nitrogen after mineralization of an aliquot of the organic phase. Octadecylamine

TABLE II

Percentage Extraction (E) of Boron with Butanol in the Presence of 2,3-Naphthalenediol and Various Organic Cations

$c(H_3BO_3) = 3.21 \cdot 10^{-3}$ mol l $^{-1}$, $c(H_2L)_{org} = c(base)_{org}^a = 5.0 \cdot 10^{-2}$ mol l $^{-1}$, $I = 0.1$, $V_{org} = V_{aq}$.

| SO_4^{2-} | | Cl^- | | ClO_4^- | |
|---------------------|------|--------|------|-----------|------|
| pH | E, % | pH | E, % | pH | E, % |
| Diphenylguanidine | | | | | |
| 2.09 | 96.6 | 2.06 | 90.1 | 2.09 | 77.5 |
| 4.48 | 89.4 | 4.49 | 80.8 | 4.62 | 69.3 |
| 8.97 | 87.2 | 9.03 | 79.0 | 9.42 | 69.2 |
| 11.10 | 75.4 | 11.09 | 74.7 | 11.09 | 67.4 |
| Tetraphenylarsonium | | | | | |
| 2.09 | 35.6 | 2.06 | 36.1 | 2.09 | 27.2 |
| 4.48 | 46.5 | 4.49 | 39.2 | 4.62 | 27.2 |
| 8.97 | 65.8 | 9.03 | 60.1 | 9.42 | 60.0 |
| 11.10 | 91.9 | 11.09 | 91.9 | 11.09 | 61.0 |
| Octadecylammonium | | | | | |
| 2.09 | 95.8 | 2.06 | 90.0 | 20.9 | 80.3 |
| 4.48 | 86.3 | 4.49 | 75.1 | — | — |
| 8.97 | 75.9 | 9.03 | 73.1 | — | — |
| 11.10 | 73.1 | 11.09 | 63.8 | 11.00 | 72.0 |

^a Diphenylguanidine and octadecylamine were used as bases (the latter in the form of saturated solution in butanol, $c < 5 \cdot 10^{-2}$ mol l $^{-1}$), tetraphenylarsonium in the form of chloride.

is almost insoluble in nitrobenzene, diethyl ether, and 4-methyl-2-pentanone (methyl isobutyl ketone). It is slightly better soluble in 1,2-dichloroethane or isoamyl acetate; during the washing of these solutions, however, emulsions are formed, which are difficult to remove. The concentration of octadecylamine in butanol was $8.5-8.7 \cdot 10^{-2} \text{ mol l}^{-1}$. The extractant was prepared by mixing a $5 \cdot 10^{-2} \text{ M}$ solution of H_2L in the corresponding solvent (or a saturated solution) with the amine solution in the vol. ratio 1 : 1. The aqueous phase contained $3.31 \cdot 10^{-3} \text{ mol H}_3\text{BO}_3/\text{l}$, pH 2.49. The recoveries in the various systems with different solvents are given in Table IV. In addition we tested the extraction with mixtures butanol-chloroform (4 : 1 to 1 : 4) and butanol-benzene (4 : 1 to 1 : 2) in the system H_2L -diphenylguanidine. The maximum recovery never exceeded that obtained during extraction with butanol only.

TABLE III

Percentage Extraction (E) of Boron with Various Solvents in the Presence of 2,3-Naphthalenediol and Various Organic Cations

$c(\text{H}_3\text{BO}_3)_{\text{aq}} = 1.65 \cdot 10^{-3} \text{ mol l}^{-1}$, $c(\text{H}_2\text{L})_{\text{org}} = 5.0 \cdot 10^{-2} \text{ mol l}^{-1}$, $c(\text{cation})_{\text{aq}} = 1.0 \cdot 10^{-2} \text{ mol l}^{-1}$, $I = 0.1 (\text{Na}_2\text{SO}_4)$, $V_{\text{org}} = V_{\text{aq}}$.

| Solvent | E (%) for pH | | | |
|---------------------------------|--------------|------|------|----------------|
| | 2.40 | 5.60 | 8.27 | 11.77 |
| $\text{Fe}(\text{phen})_3^{2+}$ | | | | |
| Nitrobenzene | — | 91.0 | 97.0 | — ^a |
| 4-Methyl-2-pentanone | — | 30.0 | 46.0 | — ^a |
| Butanol | — | 27.0 | 45.0 | — ^a |
| Dichloromethane | — | 97.0 | 99.0 | — ^a |
| $\text{Fe}(\text{dipy})_3^{2+}$ | | | | |
| Nitrobenzene | 44.7 | 81.5 | 81.0 | 95.5 |
| 4-Methyl-2-pentanone | — | 14.0 | 16.0 | — ^a |
| Butanol | 24.0 | 35.0 | 40.0 | 65.0 |
| Dichloromethane | 80.1 | 99.2 | 99.5 | 98.3 |
| Crystal violet | | | | |
| Nitrobenzene | 35.5 | 38.2 | 44.9 | — ^b |
| 4-Methyl-2-pentanone | 18.5 | 37.1 | 48.3 | — ^b |
| Butanol | 21.3 | 31.3 | 47.2 | — ^b |
| Dichloromethane | 92.4 | 92.4 | 92.7 | 83.7 |

^a Precipitate is formed; ^b emulsion is formed.

DISCUSSION

The recovery of boron as a complex with some of the compounds given in Table I should depend in the first approximation on the degree of formation of this complex, hence on the value of the equilibrium constant of that complex formation. As proved recently¹¹, the magnitude of the equilibrium constant (K) increases with increasing value of K_{a1} , the dissociation constant corresponding to the dissociation of the first proton from the two OH groups taking part in the formation of the chelate ring with boron. In fact, the recovery is governed by the extractability of the complex formed rather than by the degree of its formation. This is obvious not only from the fact that in the presence of chromotropic acid, when the highest K value occurs, only 35% of boron is extracted, but also from the comparison of the data obtained with pyrogallol and pyrocatechol. Although almost equal K values correspond to the two reagents, E is 50% higher in the case of pyrocatechol than in the case of pyrogallol. When no free hydrophilic groups (OH, SO_3H) remain, the extractability of the boron chelate formed is always higher. From this point of view, pyrocatechol and 2,3-naphthalenediol suit best. The latter can be preferred for application in extraction chromatography regarding its lower solubility in water.

Tables II and III include results found for extraction in the presence of colourless or coloured organic cations. The effect of anions of strong inorganic acids was also tested during the application of the former cations. As obvious from Table II, for any of the cations and for a fixed pH, the lowest percentage extraction appeared in the presence of perchlorates. This can be explained by a better extractability of perchlorates of the cations mentioned in comparison with the corresponding sulfates, which results in a decrease of the concentration of the cation in the aqueous phase and thus lowering of the recovery of boron. Sulfuric acid, sodium hydroxide, and sodium sulfate were therefore used in further study for adjusting the pH and the ionic strength.

While the highest percentage extraction of boron in the presence of diphenylguanidine or octadecylamine was attained at $\text{pH} \approx 2$, the optimum value for the extraction in the presence of tetraphenylarsonium is $\text{pH} \approx 11$; this is probably associated with the extractability of tetraphenylarsonium chloride itself, which is very low up to $\text{pH} 12$ (for chloroform¹⁹ and probably also for other organic solvents).

Although in the presence of any of the ferrous complex cations a complete extraction of boron can be achieved by choosing an appropriate solvent (Table III), these cations were not applied for further study of extraction separation of boron, because with their excess the aqueous phase is red coloured, which aggravates the photometric determination of boron in the aqueous phase. The application of extraction of the ionic associate $\{[\text{Fe}(\text{phen})_3]^{2+}, 2 \text{BL}(\text{OH})_2^-\}$ or $\{[\text{Fe}(\text{dipy})_3]^{2+}, 2 \text{BL}(\text{OH})_2^-\}$ for the extraction — photometric determination of boron will be the subject of the subsequent communication.

TABLE IV

Effect of Solvent on the Recovery of Boron

System: A 2,3-naphthalenediol(H_2L) + diphenylguanidine, B H_2L + tetraphenylarsonium chloride, C H_2L + octadecylamine.

| Solvent | E (%) for the system | | |
|----------------------|----------------------|-------------------|----------------|
| | A | B | C |
| Benzene | 27.5 | 25.2 ^a | — |
| 1,2-Dichloroethane | 93.3 | 44.4 | — ^b |
| Chloroform | 59.9 ^c | — | — |
| Butanol | 96.6 | 95.6 | 97.4 |
| 2-Methylpropanol | 94.6 | — | — |
| 3-Methylbutanol | 96.2 | — | — |
| Diethylether | 66.9 ^d | 35.9 | — ^e |
| 4-Methyl-2-pentanone | 66.0 | 34.6 | — ^e |
| Ethyl acetate | 76.1 | — | — |
| Isoamyl acetate | 77.3 | 31.8 | — ^b |
| Nitrobenzene | 94.6 | 38.6 | — ^e |

^a Saturated solution of diphenylguanidine and 2,3-naphthalenediol; ^b concentration of octadecylamine $< 0.1 \text{ mol l}^{-1}$, emulsion is formed during shaking with water; ^c saturated solution of 2,3-naphthalenediol; ^d saturated solution of diphenylguanidine; ^e octadecylamine is practically insoluble in this solvent.

The recoveries of boron found while using the various solvents (Table IV) cannot be correlated with any common property of the solvents (relative permittivity, dipole moment, or the solubility parameter). This is due to the complexity of the extraction system, where the recovery is governed by the solubility of more compounds than as usual for the extraction of metal chelates. Inside the various groups of solvents, however, the differences in the recoveries are not essential; butanol appeared to be the most suitable in all the three systems. The mixture of an active and an inert solvent recommended for the extraction of ionic associates²⁰ did not prove to be satisfactory in this case.

From the results obtained in this work it follows that for finding the optimum conditions for the separation of boron by means of the reversed phase partition chromatography it will be useful to study the batch extraction of boron in the system composed of 2,3-naphthalenediol as the complexing agent, diphenylguanidine (or tetraphenylarsonium chloride or octadecylamine) as the organic cation, and butanol as the solvent.

REFERENCES

1. Nikolskij B. P., Materova E. A., Valjashko M. G., Popyvkij D. S., Grekovish A. L., Anikeeva M. D.: *Sovrem. Metody Analiza, Metody Issled. Chim. Sostav i Stroenija Veshch.*, Akad. Nauk SSSR, Inst. Geochim. i Anal. Chim. 1965, 312.
2. Rjabchikov D. I., Kurilchikova G. E.: *Zh. Anal. Khim.* 19, 1945 (1964).
3. Kunin R., Preuss A.: *Ind. Eng. Chem. Prod. Res. Develop.* 3, 304 (1964).
4. Vinogradov E. E.: *Zh. Neorg. Khim.* 12, 1930 (1967).
5. Korovkin S. S., Jurkin V. B., Mironenko A. P.: *Zh. Neorg. Khim.* 11, 1910 (1966).
6. Sudo E., Ikeda S.: *Bunseki Kagaku* 17, 1197 (1968); *Chem. Abstr.* 70, 638 291 (1969).
7. Dzene A. E., Shvarc E. M., Jevinsh A. F.: *Izv. Akad. Nauk Latv. SSR, Ser. Chim.* 1970, 387.
8. Bock R., Vrchlabský M.: *Fresenius' Z. Anal. Chem.* 246, 228 (1969).
9. Gerrard N.: *Chimija Organičeskich Soedinenij Bora* (translation from English), p. 23. Chimija, Moscow 1966.
10. Bartušek M., Havelková L.: *This Journal* 32, 3853 (1967).
11. Havelková L., Bartušek M.: *This Journal* 33, 4188 (1968).
12. Havel J., Havelková L., Bartušek M.: *Chem. Zvesti* 23, 582 (1969).
13. Antikainen P. J.: *Suomen Kemistilehti* 43, B 31 (1970).
14. Antikainen P. J.: *Suomen Kemistilehti* 42, B 178 (1969).
15. Näsänen R., Tiles P., Helander P.: *Suom. Kemistilehti* 43, B 331 (1970).
16. Koch O. G., Koch - Dedic D. A.: *Handbuch der Spurenanalyse*, p. 365. Springer, Berlin 1964.
17. Eckschlager K.: *Chyby chemických rozborů*, 2nd Ed., p. 163, 174. Published by SNTL, Prague 1971.
18. Nemostruk A. A., Karalova Z. K.: *Analiticheskaja Chimija Bora*, p. 228. Nauka, Moscow 1964.
19. Marcus Y., Kertes A. S.: *Ion Exchange and Solvent Extraction of Metal Chelates*, p. 796. Wiley-Interscience, New York 1969.
20. Beschetnova E. T., Malinovskaja L. N., Golovina A. P., Zorov N. B.: *Zh. Anal. Khim.* 27, 2152 (1972).

Translated by P. Adámek.