ard sample mixtures (13) using strontium as a releasing agent. The results are shown in Table VI. Although the method has been used for the determination of calcium in other rocks and minerals, the analyses are not shown because comparative analytical data are not available. The method was especially useful for the analysis of very small samples of leucite and synthetic leucite containing very low concentrations of calcium.

CONCLUSIONS

Strontium and praseodymium have been the only releasing cations applied in actual analytical use by the author. The data available on the background emission ratios, however, indicate that a number of other cations would be more effective for analytical use.

The data presented here provide a greater flexibility in the choice of a releasing agent than was previously possible. A releasing agent may be selected on the basis of molar effectiveness, background emission, availability of reagent, or cost of reagent. The choice of a releasing agent for any specific depressant or combination of depressants should not necessarily rule out of consideration those cations which do not release calcium completely. Cations such as magnesium and beryllium can be used in analytical practice if the precaution is taken of adding the

Table	VI.	Con	narisa	n	between
Che	emical	and	Flame	Ana	lyses

	CaO, %	
Sample	Chemical (13)	Flame
N.B.S. 97 G-1 D ₂ I ₂ J ₂ K ₂ L ₃	$\begin{array}{c} 0.10 \\ 1.41 \\ 0.78 \\ 0.12 \\ 1.2 \\ 1.2 \\ 0.28 \end{array}$	$\begin{array}{c} 0.12 \\ 1.4 \\ 1.01 \\ 0.10 \\ 1.25 \\ 1.01 \\ 0.30 \end{array}$

same concentration of either of the two cations to both standard and sample. This is usually the standard practice in flame photometry. It is not always necessary, however, in the case of those elements such as strontium and lanthanum which release calcium completely. Magnesium and bervllium caused the lowest background emission ratios of any of the elements tested. Thus their use would be indicated especially in the determination of very low concentrations of calcium. Their light atomic weights enable high molar concentrations of their solutions to be prepared from relatively little reagent.

Application of the releasing effect should also be useful in the flame photometric determination of scandium, yttrium, lanthanum, and any of the

rare earth elements which have appreciable flame emissions.

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Infrared Spectrophotometric Determination of Diborane (6), Dichloroborane, and Trichloroborane in Mixtures

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► A rapid method for the determination of diborane (6) (B₂H₈, name approved by Advisory Committee on Nomenclature of Organic Boron Compounds), dichloroborane, and trichloroborane in mixtures is based upon the infrared absorption of diborane (6) at 5.35 microns, of dichloroborane at 8.98 microns, and of trichloroborane at 10.24 microns. The method possesses great advantage over wet chemical and vacuum fractionation methods in that it determines directly, without affecting the existing equilibrium of the sample, the three components present. The procedure has shown an over-all precision on synthetic samples of $\pm 2\%$ of the three compounds in the concentration ranges studied.

THIS WORK was undertaken to develop a method of analysis for mixtures containing diborane (6), dichloroborane, and trichloroborane.

Because of the inherent instability (7) of dichloroborane, vacuum fractionation methods of analysis for samples containing dichloroborane are inadequate. Wet chemical methods which determine chlorine, boron, and active hydrogen, inasmuch as they can be made accurate, are time-consuming and are not well suited for the direct determination of each component.

Infrared offers the most promising approach for the analysis of boron hydride mixtures. In this case, it is especially useful since the analysis is fast and relatively more sensitive than

wet chemical analysis because of the strong absorption in the infrared exhibited by boron compounds. The spectra of many boron hydrides and trichloroborane are available in the literature.

PRELIMINARY WORK

During the development of the analysis, several factors which in themselves were problems had to be taken into account and solved before the analysis could be made to work.

Dichloroborane could not be obtained pure since this material is highly unstable and tends to react with the formation of diborane (6) and trichloroborane. Consequently, an indirect

means had to be devised to obtain the extinction of this material in the infrared. The solution to this problem was to develop the method of analysis quantitatively in the infrared with respect to diborane (6) and trichloroborane, then to determine the infrared absorption spectrum of a mixture containing diborane (6), trichloroborane, and dichloroborane. The absorption of each compound was then measured at a chosen wave length from which the amounts of diborane (6) and trichloroborane were calculated. Simultaneously, an independent analysis for the three compounds was performed on the sample. This was accomplished through a quantitative aqueous hydrolysis of the sample with subsequent measurement of the products of hydrolysis-hydrogen, boric acid, and hydrogen chloride. In this way, the concentration of dichloroborane was determined in the sample, and this value was related to the absorption of this compound in the infrared, whereby the absorptivity for the compound was calculated. The procedure of analysis and tables comparing analyses of typical samples are given (see Table I).

The compounds, particularly trichloroborane, react immediately with the sealing wax which is used to prepare the vacuum infrared cells in which the analysis is run. The reaction of trichloroborane with waxes appears to be general; various waxes and sealers were tried without success. To obviate this problem, a new technique was developed for the preparation of vacuum infrared cells which entails lapping the sodium chloride windows to the cell body to form a vacuum seal.

The cell consists of a 5-cm. (\pm 0.1 mm.) length of 40-mm. outside diameter borosilicate glass tubing to which an inlet has been attached which contains a 4-mm. vacuum stopcock and a 12/30 standard taper female joint. The windows of the cell are 49.5 \times 6.5 mm. sodium chloride optics obtained from Perkin-Elmer Instrument Corp., Cat. No. 027-1105. The cell is contained in a carriage also obtained from the above supplier, Cat. Nos. 012-1379, 012-1380, and 012-1387.



Figure 1. Vacuum sampling system

- 1. McLeod gage
- 2. Du Brovin gage
- 3. Waste trap 4. Mercury bubb
- 4. Mercury bubble off 5. Manometer full scal
- Manometer full scale
 Mercury diffusion pump
- 7. Sample bulb
- 8. Vacuum pump
- 9. Trap 10. IR cell
- 11. IR spectrophotometer

To assemble the cell, the parallel ends of the cell body are ground on a flat plate with No. 600 emery until a near-optical finish is obtained. The windows are affixed to the cell and held in position by the carriage. The unit is attached to a vacuum system and leaks are detected with the aid of a discharge coil. Any leaks are sealed by forming a bead of wax at the juncture of the cell and the sodium chloride windows with hot tackiwax while the cell is in a fixed position. If necessary, the cell is warmed while pumping on the cell to facilitate sealing, although this is not often necessary. The finished cell should contain no wax on the inside of the cell and should be capable of holding a 10⁻⁵-mm. Hg pressure for several hours or more.

EXPERIMENTAL

Apparatus and Reagents. Spectrophotometer, Perkin-Elmer Model 21. Infrared gas cell, 5-cm. path length. Vacuum sampling system (Figure 1). Trichloroborane, Matheson technical

grade. Diborane (6), Olin Mathieson, research grade.

Dichloroborane, experimental sample. Purification of Reagents. Trichloroborane was purified by cold trap fractionation on a vacuum rack. The material from the cylinder was condensed into a cold trap (acetonedry ice) and pumped upon for 15 minutes to free the material from volatile impurities. The material was then warmed, recondensed, and again pumped on to exclude entrained impurities. This procedure yielded trichloroborane of 99.8% purity based on chloride and orthoboric acid determinations.

Diborane (6) was purified similarly by vacuum cold trap fractionation. The material was condensed with caution into a liquid nitrogen trap from a cylinder which was contained in an acetone-dry ice bath. Hydrogen and other volatile impurities were pumped off. The condensate was warmed and again cooled, after which the material was again pumped upon. This procedure yields 97.0% diborane (6), based upon active hydrogen and orthoboric acid determinations.

Dichloroborane was not purified. The sample used contained diborane (6) and trichloroborane. The purity of the sample was ascertained by active hydrogen, chloride, and orthoboric acid analysis. Multiple analyses were run and an average value was determined.

Procedure of Analysis. The sample, which is usually submitted contained in a 500-cc. gas sampling bulb, is attached to the vacuum analysis rack at A (Figure 1). The infrared cell is placed in position on the instrument and connected to the vacuum system at B. The system, including the cell, is pumped down to 10^{-4} mm. and checked for leaks.

Sampling is accomplished by opening the sample stopcock and allowing the sample to share into the cell until a pressure of approximately 100 mm. registers on the manometer. At this point, both the sample and infrared cell stopcocks are closed, the exact pressure is determined from the manometer, and the infrared spectrum of the sample is determined. No corrections for variance in temperature are required, providing the temperature fluctuation does not exceed $\pm 2^{\circ}$ C. The absorptions at 5.35, 8.98, and 10.24 microns are measured from 5.10 microns and from the blank base line, respectively, for diborane (6), dichloroborane, and trichloroborane. These values are sub-



Figure 2. Infrared spectra of dichloroborane and trichloroborane



Figure 3. Infrared spectrum of diborane (6)

stituted into the equations given below, from which percentage composition can be calculated. Several runs are made for each analysis to eliminate inherent errors such as nonhomogeneity of the sample and instrument reproducibility. After the analysis, the contents of the vacuum system are exhausted to a hood system.

DISCUSSION

Diborane (6) has been studied (1, 6)and determined (3) in mixtures of tetraborane (4), pentaborane (9), and pentaborane (11). The analysis method for diborane (6) reported by McCarty (3) is not desirable, owing to the fact that the analytical absorption band at 6.15 microns which was chosen for analysis is pressure sensitive. It has been determined at this laboratory that all of the absorption bands of diborane (6) are pressure sensitive; under 200mm. total pressure, the one least affected being a terminal B--H stretch at 5.35 microns. This band has a weak absorption; however, it has been demonstrated to be the one which is most accurate for diborane (6) determination in the presence of trichloroborane and dichloroborane, which do not appear to be similarly affected. The infrared spectrum of dichloroborane containing trichloroborane shown in Figure 2 is in perfect agreement with the assignments for dichloroborane in the literature (5). This spectrum represents the material obtained from a mixture of diborane (6), trichloroborane, and

dichloroborane after flashing in vacuum at -78° C. to remove diborane (6). The spectrum represents a material consisting of 27.7% BHCl₂ and 72.1% BCl₃. Dichloroborane is characterized in the infrared by a weak single absorption at 2600 cm.⁻¹ and two strong doublets at 1098, 1084 cm.⁻¹ and 898, 885 cm.⁻¹ which are due to B—Cl stretching. This compound is easily distinguished from chlorodiboranes by the absence of strong terminal BH2 and bridge B-H-B vibrations at the regions of 2600 and 1600 cm.⁻¹, respectively. One minor absorption occurs at 1580 cm.⁻¹ which could be attributed to B-H-Cl.

The infrared spectra of diborane (6), trichloroborane, dichloroborane, and trichloroborane, and a mixture of boranes are shown in Figures 3 to 5. These spectra were obtained using the vacuum system associated with the infrared spectrophotometer (Figure 1) to measure all samples: the infrared absorptions of the purified trichloroborane and diborane (6) were determined by themselves and in mixtures at several different pressures. From inspection of these spectra, it is observed that trichloroborane, diborane (6), and it will be shown later, also dichloroborane have somewhat mutual absorption bands in the regions most likely to be used for analysis. Consequently, this method of analysis is set up employing Vierordt's method (2) - using simultaneous equations to correct for "overlapping" absorption. It was determined from working with this system that the best choice of wave length for diborane (6) was at 5.35 microns (measured from 5.10 microns) and for trichloroborane at 10.24 microns (measured from blank base line). The most obvious choice for diborane (6) is at 6.15 microns; however, as mentioned above, experimental work at this wave length has shown diborane (6) to be pressure sensitive. Because diborane (6) exhibits a B-H-B bending vibration at 10.26 microns, the region of major absorption of trichloroborane, the analytical wave length for trichloroborane was taken at 10.24 microns. At this point, diborane (6) does not interfere significantly with the determination of trichloroborane at usual pressures. From this work and at these wave lengths, absorption coefficients have been calculated. They are tabulated below:

$\alpha^{25^{\circ}}$ C. BCl ₃ 10.24 $\mu = 0.01669$
α^{25} ° ^C · BCl ₃ 5.35 μ = 6.70 × 10 ⁻⁵
$\alpha^{25^{\circ}}$ C. B ₂ H ₆ 10.24 μ = 3.33 \times 10 ⁻³
$\alpha^{25^{\circ}}$ C. B ₂ H ₆ 5.35 μ = 2.90 \times 10 ⁻³
absorbance
where α = pressure in mm. in 5-cm. cell

Mixtures of diborane (6) and trichloroborane were made and the infrared absorptions at 5.35 and 10.24 microns determined. Using the following calculations, the percentage composition of synthetic samples was determined. The results are expressed in Table I.



Figure 4. Infrared spectrum of trichloroborane



Figure 5. Infrared spectrum of mixture of diborane (6), trichloroborane, and dichloroborane

Abs._{5.35 μ} (Absorbance) =

$$P_{\mathrm{B}_{2}\mathrm{H}_{6}} \begin{pmatrix} \mathrm{B}_{2}\mathrm{H}_{6} \\ \alpha_{5\cdot35 \ \mu} \end{pmatrix} + P_{\mathrm{BCl}_{3}} \begin{pmatrix} \mathrm{BCl}_{3} \\ \alpha_{5\cdot35 \ \mu} \end{pmatrix}$$

Abs._{10.24} μ (Absorbance) =

$$P_{\mathrm{B}_{2}\mathrm{H}_{6}}\left(\frac{\mathrm{B}_{2}\mathrm{H}_{6}}{\alpha_{10\cdot24\,\mu}}\right) + P_{\mathrm{B}\mathrm{Cl}_{4}}\left(\frac{\mathrm{B}\mathrm{Cl}_{3}}{\alpha_{10\cdot24\,\mu}}\right)$$

where P = pressure in mm. in 5-cm.cell.

To extend the method to include dichloroborane, a sample containing unknown quantities of diborane (6), trichloroborane, and dichloroborane was introduced into a 5-cm. infrared cell, and the infrared spectrum of the mixture was determined. Tentatively, employing the assumption that dichloroborane does not absorb at 5.35 and at 10.24 microns, the quantities of diborane (6) and trichloroborane were determined using the above equations and absorption coefficients. Simultaneously, and on the sample used for infrared analysis, the sample was analyzed by the hydrolysis method (4). Correcting the values for hydrogen, chloride, and boron for that which is contained in the sample by the previously determined amounts of diborane (6) and trichloroborane, the concentration of dichloroborane in the sample was based on the following equations:

$$B_2H_6 + 6H_2O \rightarrow 6H_2 + 2B(OH)_2$$

$$BCl_3 + 3H_2O \rightarrow 3HCl + B(OH)_3$$

 $BHCl_2 + 3H_2O \rightarrow H + B(OH)_3 + 2HCl$ moles of $BHCl_2 = moles H_2 -$

 $6(\text{moles } B_2H_6)$

Relating the concentration of dichloroborane to the B-Cl absorption of this compound at 8.98 microns, an absorption coefficient was calculated. An average value was

$$2.055 \times 10^{-2}$$
 at 25° C

Samples of the dichloroborane mixture containing known amounts of additional diborane (6) and trichloroborane were analyzed similarly, and dichloroborane had no significant absorption at 5.35 and 10.24 microns, thereby confirming the original supposition.

The only factors left to be determined were the absorption coefficients of diborane(6) and trichloroborane at 8.98 microns. These data, with the other absorption coefficients, were set up in the following equations for the analysis:

$$Abs_{.5\cdot35 \mu} = \left(P_{B_{2}H_{6}}\right) \left(\begin{array}{c}B_{2}H_{6}\\\alpha_{5\cdot35 \mu}\end{array}\right) + \left(P_{BCl_{3}}\right) \left(\begin{array}{c}BCl_{3}\\\alpha_{5\cdot35 \mu}\end{array}\right) + \left(P_{BHCl_{2}}\right) \left(\begin{array}{c}BHCl_{2}\\\alpha_{5\cdot35 \mu}\end{array}\right) \\ Abs_{.10\cdot24 \mu} = \left(P_{B_{2}H_{5}}\right) \left(\begin{array}{c}B_{2}H_{6}\\\alpha_{10\cdot24 \mu}\end{array}\right) + \left(P_{BCl_{3}}\right) \left(\begin{array}{c}BCl_{3}\\\alpha_{10\cdot24 \mu}\end{array}\right) + \left(P_{BHCl_{2}}\right) \left(\begin{array}{c}BCHl_{2}\\\alpha_{10\cdot24 \mu}\end{array}\right) \\ Abs_{.8\cdot98 \mu} = \left(P_{B_{2}H_{6}}\right) \left(\begin{array}{c}B_{2}H_{6}\\\alpha_{8\cdot98 \mu}\end{array}\right) + \left(P_{BHCl_{2}}\right) \left(\begin{array}{c}BHCl_{2}\\\alpha_{8\cdot98 \mu}\end{array}\right) + \left(P_{BHCl_{2}}\right) \left(\begin{array}{c}BHCl_{2}\\\alpha_{8\cdot98 \mu}\end{array}\right) + \left(P_{BHCl_{2}}\right) \left(\begin{array}{c}BHCl_{2}\\\alpha_{8\cdot98 \mu}\end{array}\right) + \left(P_{BHCl_{2}}\right) \left(\begin{array}{c}BHCl_{2}\\\alpha_{8\cdot98 \mu}\end{array}\right) + \left(\begin{array}{c}BHCl_{2}\\\alpha_{8}\\\alpha_{8}\otimes9 \mu}\end{array}\right) + \left(\begin{array}{c}BHCl_{2}\\\alpha_{8}\otimes9 \mu}$$

The following formulas are derived by

substituting coefficients and solving for P in the above equations:

 $P_{B_2H_1}$ in mm. = $(\text{Abs.}_{5\cdot35~\mu}\times\,10^3)$ $(16.69) - (Abs._{10.24 \ \mu} \times 10^3) (0.067)$ 48.18 P_{BCl_3} in mm. =

$$\frac{(\text{Abs.}_{10.24 \ \mu} \times 10^3) - 3.33P_{\text{B}_2\text{H}_6}}{16.69}$$

 P_{BHCl_2} in mm. =

$$\frac{(\text{Abs.}_{8\cdot98}\,\mu\times10^3)-0.010P_{\text{B}_2\text{H}_6}}{20.55}$$

Table II indicates typical results achieved using the infrared method of analysis.

LIMITATIONS OF METHOD

The method suffers loss of accuracy for diborane (6) when the sample contains a trichloroborane-to-diborane (6)

	Table I.	Percentage	Composition	of Syntheti	c Samples	
Synth	etic Mixture,	Mm.	Analysis	Mm.	Recover	y, %
B_2H_6	BCl ₃	N_2^a	B_2H_6	BCl ₃	B_2H_6	BCl ₃
9.25	84.00	0	9.0	82.6	97.3	98.3
11.20	108.90	Õ	11.5	109.3	102.7	100.5
4.24	41.21	Ó	4.0	40.6	94.3	98.8
1.59	15.45	Õ	ca. 1.0	15.6	62.8	101.4
31.60	0	Ō	31.4	0	99.4	
31.60	45.00	Õ	31.0	44.5	98.1	98.9
23.30	14.00	Õ	23.3	14.4	100.0	102.9
77.10	14.00	Õ	78.0	14.4	101.2	102.9
45.30	18.00	137.6	45.7	18.3	100.9	101.7

Av. per cent recovery of B_2H_6 = 99.2 Av. per cent recovery of BCl_3 = 100.7

^a This column included to show that the analysis is not affected by pressure.

			Table II	. Typic	al Results				
Mintunoa	Ar	alysis by	Infrare	d	Mixture ^a Mm_in	Anal	ysis by Met	Wet Che thod	mical
Mm in 5-	Sample No.			5-Cm.	Sample No.				
Cm. Cell	1	2	3	4	Cell	1	2	3	4
B₂H6 BCl₃ BHCl₂ % Total	$14.10 \\ 56.92 \\ 26.10 \\ 97.12$	$15.45 \\ 62.50 \\ 22.05 \\ 100.00$	$12.30 \\ 63.90 \\ 23.20 \\ 99.40$	$14.59 \\ 54.28 \\ 31.13 \\ 100.00$	$egin{array}{c} B_2H_6\\ BCl_8\\ BHCl_2 \end{array}$	$\begin{array}{r} 14.70 \\ 56.28 \\ 28.99 \\ 99.97 \end{array}$	$14.98 \\ 61.70 \\ 22.21 \\ 98.89$	$\begin{array}{c} 12.42 \\ 63.51 \\ 23.10 \\ 99.03 \end{array}$	$\begin{array}{r} 14.10 \\ 53.70 \\ 31.94 \\ 99.74 \end{array}$

 $^{\circ}$ These mixtures were made up by adding measured amounts of B_2H_6 and BCl_3 to a sample of HBCl₂ containing BCl₃ which had been previously analyzed by the wet hydrolysis method.

ratio greater than 10 to 1. This fact is attributed to the absorption of trichloroborane at 5.35 microns, which in this case becomes larger than the absorption of diborane which is being measured. It is suggested that for samples containing small amounts of diborane (6) in the presence of large quantities of trichloroborane the wave length of 6.15 microns be used. Even though this band is pressure sensitive, quantitative work can be accomplished by always maintaining a constant pressure in the cell with nitrogen and operating above 200-mm. total pressure.

In samples containing diborane (6)to-trichloroborane ratios of 2.5 to 1, a shift in the infrared absorption at 10.24 microns occurs with the appearance of a small shoulder at 10.25 microns. In this instance, a small loss of accuracy is experienced. It has been the practice with such samples to take measurements at the shoulder. These values are no better than $\pm 5\%$ with respect to the trichloroborane.

General interference with the analysis can be expected by the presence of compounds containing boron-hydrogen and/or boron-chlorine linkages.

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Causes and Control of Matrix Effects in Spectrographic Discharges

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In quantitative spectrographic analysis, changes in sample matrix can change analytical intensity ratios independent of element concentrations and cause large errors. Changes in the discharge temperatures that result from matrix changes were measured and found to explain the observed ratio changes. A new equation accounts for these temperature changes and defines new minimum requirements for matching line pairs. Interpretation of results based on this equation shows that changes in intensity ratio with matrix are a natural consequence of a poor choice of internal standard, that the best choice can be made only by deliberately varying the discharge temperature, and that when a choice less than perfect is necessary, a temperature correction improves results. Matrix effects due to collisions of the second kind, which would not be corrected for, were not observed for the sensitive lines used.

I N QUANTITATIVE SPECTROGRAPHIC ANALYSIS, line intensities that are used to measure element concentrations are affected profoundly by the sample matrix. Differences in composition between standards and samples can produce large errors usually attributed to matrix, interelement, or extraneous element effects. Composition differences in the matrix cause the intensities of the minor constituent lines to change independently of concentration, and the intensities of different lines to be affected differently. Intensity ratios are likewise adversely affected.

To avoid these effects, samples must resemble calibration standards. Similar compositions are obtained by preparing calibration standards to match each sample, which takes time, or by heavy dilution of both standards and samples, which reduces sensitivity. Maximum sensitivity without time-consuming calibrations has not been possible.

A spectrochemical series (6), electrodes of modified shape (1), and a total-arcing method (19) have been used in attempts to overcome matrix effects. A temperature correction that had been used successfully for other purposes was also suggested (1,4), but it was claimed to be unnecessary with stable sources (9) presumably with a constant matrix. The complexity of the problem is illustrated by Ahrens' list of composition-dependent factors that can influence line intensities (2). The problem is simplified, however, for an idealized combination of sample and discharge source. In such a system, the matrix is important only insofar as it regulates the discharge temperature. Although the matrix effects predicted for such a system are minimum effects,

they must be examined first before other factors can be assessed.

THEORETICAL

In an ideal sample, the partial pressure of each constituent depends on its concentration in the condensed phase and the vapor pressure of the pure constituent. In an ideal source, the sample and discharge are a closed system at a single temperature, and all phases and energy states are in equilibrium.

For thermal excitation in an idealized system, the discharge temperature determines the concentration of an excited state, according to the Boltzmann equation:

$$p^* = p_o \exp - E/kT_m$$

Under constant source conditions, the temperature is determined by the effective ionization potential of the discharge gases (3). Therefore, the matrix de-termines temperature, T_m , and hence, p^* , the concentration of particles in the excited state. From Henry's or Raoult's law, $p_o = f P_o$, and, from the Clausius-Clapeyron equation,

$$P_o = B \exp - \Delta H / k T_m$$

Hence,

 $p^* = fB \exp - (\Delta H + E)/kT_m$