or, better, that the equilibrium in these cases is too far to the left for the reaction to be used for analytical purposes. No inflection points in the titration curves could be obtained for acetaldehyde, propionaldehyde, or butyraldehyde. Cinnamaldehyde is peculiar in this respect in that it is essentially an aliphatic aldehyde with the phenyl group on the chain, yet it will react completely enough to be used. Crotonaldehyde, which is similar to the cinnamaldehyde except that the phenyl group is replaced with a methyl group, does not show any titration break at all.

Since aldehydes are difficult to obtain in a pure form, difficult to purify, and difficult to keep in a pure form, this study was limited to the aldehydes indicated in Table I and in the text. The aldehydes chosen were those which occur most commonly and which should adequately illustrate the extent of applicability of the method.

### REAGENTS AND EQUIPMENT

**Lauryl Amine Solution.** Two moles of lauryl amine were dissolved in 1 liter of ethylene glycol–2-propanol mixture. Lauryl amine was purchased as Armeen 12D from the Chemical Division of Armour & Co.

**Salicylic Acid.** A 1 *N* solution in ethylene glycol–2-propanol was standardized against alcoholic sodium hydroxide.

**Equipment.** Glass, calomel electrodes were used, along with a model H-2 Beckman pH meter.

### PROCEDURE

A 0.02 mole sample of the aldehyde is weighed into a 100 or 150-ml. glass-stoppered flask. Exactly 20 ml. of the lauryl amine solution is added, the cover is replaced, and the mixture is shaken for a few minutes. The mixture is allowed to stand for 1 hour. The solution is then transferred with ethylene glycol-2-propanol to a 250-ml. beaker, and the excess lauryl amine is titrated potentiometrically with 1 *N* salicylic acid.

A blank is also run.

### CALCULATION

$$\frac{(\text{Blank} - \text{titration}) \times N_{\text{salicy}} \times \text{M.W.}}{\text{gram sample} \times 1000} \times 100 = \%\ \text{aldehyde}$$

### ACKNOWLEDGMENT

Acknowledgment is made to Dale Eichlin who ran some of the check experiments to establish the validity of the method.

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Received for review October 18, 1952. Accepted January 28, 1953.

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# Direct Volumetric Assay of Sodium Borohydride and Potassium Borohydride

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Analysis of compounds, including the borohydrides, for hydride hydrogen has conventionally been carried out by causing reaction with an alcohol, water, or dilute aqueous acid, and measuring the volume of hydrogen gas evolved at constant pressure, or the pressure at constant volume. A recently reported volumetric method (*3*) of sodium borohydride assay has employed oxidation with an excess of standard iodate and, after conversion of the excess to iodine, back titration with thiosulfate.

The method described herein involves the direct titration of a sodium or potassium borohydride solution with standard sodium hypochlorite, using Bordeaux red as an indicator. The stoichiometry is in accord with the following equation:

$$H^+ + BH_4^- + 4\ OCl^- \longrightarrow H_3BO_3 + 4Cl^- + H_2O$$

The pH of the solution during the titration is critical, having an optimum value in the range 9.6 to 10.3. Carbonate buffer is used to maintain the proper pH.

### REAGENTS

**Sodium Hypochlorite, 0.1 *N*.** A convenient method is to dilute 115 ml. of a commercial 5% sodium hypochlorite solution to about 2 liters with water. Clorox was used, although there seems to be no reason why other brands would not be satisfactory. The solution was standardized against standard arsenite using Bordeaux red (*1, 2*).

**Carbonate Buffer Mixture.** To a mixture of 50 grams of potassium bromide and 100 grams of sodium bicarbonate in about 600 ml. of water was added 6 *N* sodium hydroxide (about 130 ml.) until the pH was 9.6 (pH meter). The solution was diluted to about 1 liter.

**Sodium Hydroxide, 2 *N*.**

**Bordeaux Red Indicator Solution.** Two tenths of a gram of Bordeaux red (National Aniline and Chemical Co., Inc.) was dissolved in 100 ml. of water.

### PROCEDURE

Five milliliters of 2 *N* sodium hydroxide is introduced into a dry 100-ml. volumetric flask using a funnel to avoid wetting the upper neck with the base. The flask (without stopper) and contents are tared, a quantity of sodium or potassium borohydride about the size of a large pea is added, and another weighing is made. The weight of borohydride should be between 0.1 and 0.3 gram. The volume is made up to 100 ml. with distilled water.

**Table I. Analysis of Sodium Borohydride and Potassium Borohydride**

(Comparison of hypochlorite method and hydrogen evolution method)

| Sample | % Borohydride | |
|---|---|---|
| | Hypochlorite | Hydrogen Evolution |
| $NaBH_4$ | 84.3, 83.8, 83.6 | 85.0, 84.6 |
| $NaBH_4$ | 83.9, 83.7 | 84.4, 82.9 |
| $KBH_4$ | 93.9, 93.6 | 95.3, 95.1 |
| $KBH_4$ | 92.8, 92.3, 92.6 | 93.3, 94.2 |

Ten milliliters of the carbonate buffer mixture and 10 to 15 ml. of water are introduced into a titration vessel. A 5-ml. aliquot of the borohydride solution and two drops of Bordeaux red indicator solution are added, and the solution is titrated with standard sodium hypochlorite. The red solution becomes increasingly blue during the course of the titration until just before the end point, when it is almost a pure blue. The end point is marked by a sharp change from blue to yellow-green.

The per cent borohydride in the sample taken is given by:

$$\frac{(\text{Ml. of NaOCl} \times N) \times \text{meq. wt. of borohydride} \times 100}{\text{grams of sample in 5-ml. aliquot}}$$

The milliequivalent weight of sodium borohydride is 0.004731 and of potassium borohydride is 0.006744.

## RESULTS

A representative set of analyses for two samples of sodium borohydride and two of potassium borohydride is given in Table I. The results of parallel determinations, by the hydrogen evolution method, on aliquots of the same solutions are given.

In general, the results by hypochlorite analysis have averaged about 1% lower than the results by analysis of the same samples using the hydrogen evolution method.

## DISCUSSION

**Use and Stability of Hypochlorite.** The use of hypochlorite solutions in volumetric analysis has been evaluated and encouraged by Kolthoff and Stenger (*2*). Although the calcium salt is recommended over the sodium salt because of its greater stability, it is the author's experience that diluted solutions of commercial sodium hypochlorite do not require restandardization more often than once a week when stored in a brown bottle out of direct sunlight. Moreover, the solutions are far easier to prepare and, during a titration, no precipitate of calcium carbonate is formed. While the precipitate does not alter the perception of the end point, it detracts from its striking character in the borohydride titration.

As recommended by Kolthoff and Stenger for the hypochlorite-arsenite titration, an excess of bromide ion has been provided in the titration mixture, through incorporation with the carbonate buffer. Its function is to exploit the increased reaction rate of hypobromite (formed instantly by reaction of bromide with hypochlorite) while avoiding its instability in solution. Bromide has likewise been found essential in the borohydride titration.

**Borohydride Solution.** Aqueous borohydride solutions are most stable in highly alkaline solutions. Inappreciable decomposition occurs in 2 or 3 hours in the solutions prepared as directed above.

**Effect of pH during Titration.** Above pH 10.3 the rate of reaction of hypochlorite (hypobromite) with borohydride is too slow for a satisfactory end point while much below pH 9.6 a slight but significant fraction of borohydride will decompose during the minutes of the titration. Thus, while the solution of the borohydride sample is stable for hours because of its high pH (around 12), addition of the buffer mixture lowers the pH to around 10 and so the solution should be titrated within 10 to 15 minutes in order to avoid significant decomposition.

**Indicator Action.** Kolthoff and Stenger reported that Bordeaux red is an irreversible indicator in the titration of arsenite with hypochlorite. The color change is given as pink to light yellow-green.

Somewhat different color changes, observed under the conditions of the titrations reported here, are consistent with the following schematic representation:

$$\text{Red} \xrightarrow{\text{OCl}^-} \text{blue} \underset{\text{BH}_4^-}{\overset{\text{OCl}^-}{\rightleftharpoons}} \text{yellow-green} \xrightarrow[\text{slow}]{\text{OCl}^-} \text{colorless}$$

Thus, during a titration of borohydride with hypochlorite the red color becomes progressively bluer, with the rate of change increasing rapidly as the end point nears. At the end point, the color changes sharply to yellow-green and, if allowed to stand a few minutes, gradually fades. If, immediately upon reaching the yellow-green end point, a few drops of borohydride solution is added, the color will revert to a pure blue which can again be converted to yellow-green on addition of excess hypochlorite.

During the titration of arsenite with hypochlorite, a tendency toward blue is sometimes observed. Since the color changes are irreversible throughout, the amount of blue formed depends on the timing of the addition of drops of indicator as the titration progresses.

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RECEIVED for review December 29, 1952. Accepted February 19, 1953.

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# Determination of Thoron in Mineral Waters

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A SIMPLE method for the direct determination of thoron ($Rn^{220}$) in mineral waters (lower limit of the method $10^{-9}$ to $10^{-10}$ curie per liter) is described. The proposed method gives the actual ratio of thoron to radon in mineral waters, whereas the induced activity method, in which the decay products of thoron and radon are deposited on a charged wire, only gives the ratio in the atmosphere near the orifice of the mineral waters. The value obtained by the induced activity method is much lower than the actual ratio of thoron to radon in the mineral water, due to the decay of the short-lived thoron (54.5 seconds).

Numerous papers are available on the determination of radon in mineral waters, but practically nothing has been done on the quantitative determination of thoron in mineral waters, because of the difficulties in measuring the radioactivity of a gaseous isotope with a half life of only 54.5 seconds.

Along with the ever-growing interest in the geochemistry of uranium and other radioactive elements, the demand for simple and accurate determinations of the radioactive elements, especially short-lived elements in mineral waters, has increased. It is sometimes very important to know quickly whether the radioactivity of mineral waters is mainly due to the uranium or thorium series; the determination of radon and thoron gives a simple solution for this problem.

The radon contents of sea water, river water, rain water, and drinking water are of the order of magnitude of $10^{-11}$ to $10^{-13}$ curie per liter, whereas well water, mineral water, and hot spring water often contain much higher amounts of radon and radium, as shown in Table I.

As early as 1909, Schlundt and Moore (*25*) showed the presence of thoron in hot spring gases in Yellowstone National Park. They found Terrace Spring No. 2 contained 15 times as much thoron as radon, but their work was of a qualitative nature, and they did not determine thoron in hot spring waters. Studies on the thoron in mineral waters and gases were carried out by Lester (*21*), Lepape (*17–20*), Proix-Noe and Proix (*23*), Hsü and Hsieh (*8*), Cluzet and Chevallier (*2*), Andrade (*1*), Shchepot'eva (*26*), Iwasaki, Ishimori, and Hatae (*10*), Kamada (*11*), and Shimokata (*27*). Gübeli and Kolb (*6*) have recently described a circulating method for determining radon and thoron in waters.

As already reported elsewhere (*14, 16*), the radon isotopes are often contained in natural waters in large excess to the equilibrium amounts of the parent elements (radium isotopes). Table II