ANALYSIS OF MIXTURES OF GLYCOLS BY ION-EXCHANGE CHROMATOGRAPHY

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In previous reports, the authors have developed a procedure for the determination of polyols by dichromate oxidation[1], and investigated the elution behavior of the glycols with the application of the plate theory of ion-exchange chromatography[2,3]. An equation describing the elution behavior of the glycols was derived[2]

$$\frac{WQ[RBO_2]}{CV} = \frac{K_1[BO_2^-]}{K_2} + \frac{1}{K_2}$$

where W is the weight of the resin in grams, Q is the exchange capacity per gram of resin, $[RBO_2]$ is the mole fraction of the resin in the borate form, C is the distribution ratio of the glycol[2], and V is the interstitial volume of the column of resin. The equation was used to evaluate the complexing constants K_1 and K_2 for the reactions between the glycol and the borate ion in solution and on the resin respectively. Then the elution equation and the complexing constants were used to calculate the conditions necessary for the separation of diethylene glycol, ethylene glycol, 1,2-propylene glycol, the *meso* and the dl isomers of 2,3-butylene glycol, and glycerol[3]. In this paper, experimental procedures and analytical results of the method chosen for the analysis of a glycol mixture are reported.

APPARATUS AND REAGENTS

Apparatus for the collection of small fractions of column effluent has been described[4].

Absorbance measurements were made with a Beckman quartz spectrophotometer, Model DU, equipped to receive 10-cm silica cells.

Two columns with an internal cross-sectional area of 2.28 sq. cm were used. The first was filled with 76.5 cm of Dowex 1-X8, 200-300 mesh, which had previously been converted to the borate form. The second was similarly packed with 20 cm of Dowex 1-X8 that had been equilibrated with 0.020M solution of borax (sodium tetraborate decahydrate).

Two eluants were required for analysis. The first 0.925M with $NaBO_2$ and 0.0004$\pm$0.0002M with sodium hydroxide. (The quantity of sodium hydroxide was determined by the saturation of a portion of eluant with mannitol and the potentiometric titration with hydrochloric acid to a pH of 9.2.) The second eluant was a 0.020M solution of borax.

The resin, Dowex 1-X8, 200-400 mesh (dry-screened) was wet-screened through 200 mesh to remove the fine particles which cause a large pressure drop. The resultant resin, approximately 200-300 mesh (when dry) was converted to the desired form before use. In order to avoid the use of large quantities of the eluants, all of the resin was converted from the chloride to the hydroxide form by the passage of 20 ml of 5M carbonate-free sodium hydroxide per meq of resin. Portions of the resin were then easily converted to the borate and borax forms by the passage

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of either 0.925*M* sodium borate or 0.020*M* borax in an amount which contained three times the number of milliequivalents of resin.

A column of 80 cm × 2.28 sq. cm was packed with 76.5 cm of the converted resin by pouring the resin, slurried with the 0.925*M* sodium borate eluant into the column and draining off the excess solution. One liter of the eluant was passed through the column at the maximum flow rate to insure complete packing of the resin. Another column of 25 cm × 2.28 sq. cm was similarly packed with 20.0 cm of resin which had been previously equilibrated with 0.020*M* borax.

Stock solutions of the glycols, approximately 2*N* as reducing agents, were prepared and standardized by the recommended procedure. Diethylene glycol (DEG), ethylene glycol (EG), and 1,2-propylene glycol (PG) were obtained from Eastman and used without further purification. Glycerol (GL) from J. T. Baker Chemical Company was also used without further purification. Three samples of 2,3-butylene glycol (BG) were used. The first from E. I. du Pont de Nemours was a mixture of *meso* (*m*) and dl isomers. The second from the National Research Council of Canada was found to be a mixture of *meso* and *l* isomers. The third sample, technical 2,3-butylene glycol from the Celanese Corporation of America, was chromatographed and found to be a mixture of 95.0% *meso* and 3.2% dl isomers with 1.8% (based on the reducing capacity) of an oxidizable impurity of undetermined nature.

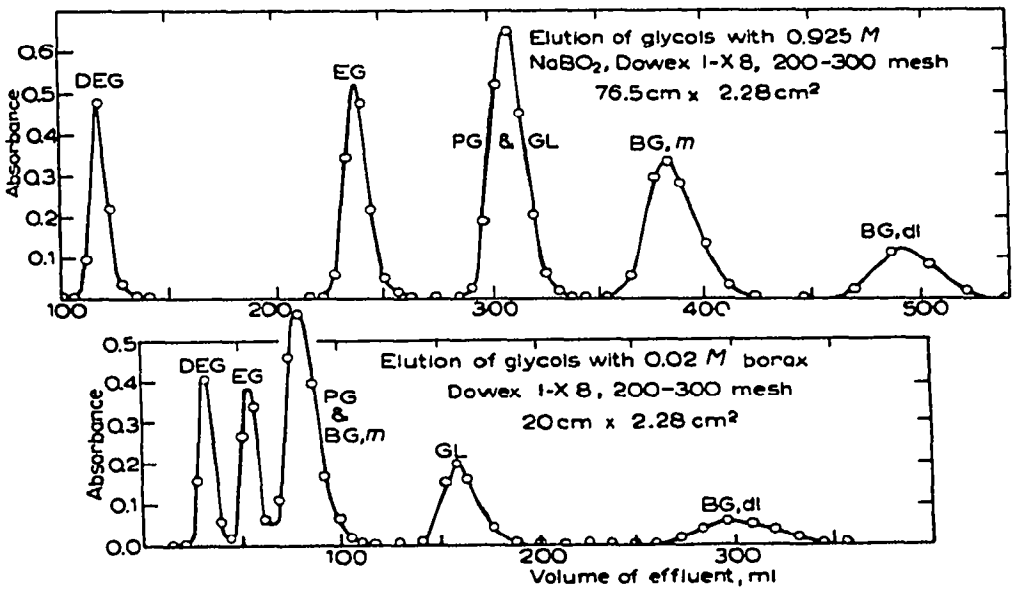

Fig. 1.

ELUTION GRAPHS

Figure 1 represents the quantitative separation of diethylene glycol, ethylene glycol, 1,2-propylene glycol, the *meso* and the dl isomers of 2,3-butylene glycol, and glycerol. Under these conditions, two elutions furnish all the data that are needed for the complete analysis of a mixture which contains the six glycols mentioned above. The elution graphs were obtained by the collection of small fractions with a fraction collector, The fractions (usually 6 ml) were mixed with a constant volume (usually 5 ml) of oxidizing reagent[1], cooled, and diluted with 25.00 ml of water before measurement of the absorbance at 610 mμ against a blank (a fraction, which is known not to contain a glycol, mixed with the oxidizing reagent and diluted).

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METHOD OF ANALYSIS

The sample was dissolved in water. An aliquot of 2 ml containing in general, not more than 10 mg of any one glycol was carefully transferred to the top of the resin bed. The sample was drained at a flow rate of 0.5 cm per minute into a 100-ml graduated cylinder. Two 2-ml portions of the eluant were used to wash down the inside of the column. The sample was then eluted at a flow rate of 0.5 cm per minute. The effluent from the elution with 0.925*M* sodium borate was collected in successive fractions of 100, 60, 60, 60, 70, 95, and 95 ml. These contain, respectively, blank, diethylene glycol, blank, ethylene glycol, a mixture of 1,2-propylene glycol and glycerol, the *meso* isomer of 2,3-butylene glycol, and the dl isomers of 2,3-butylene glycol. The effluent from the elution with 0.020*M* borax was similarly collected in successive fractions of 125, 75, 55, 95, and 35 ml. The first fraction which contained diethylene glycol, ethylene glycol, 1,2-propylene glycol, and the *meso* isomer of 2,3-butylene glycol was discarded. The second, third, fourth, and fifth fractions contained, respectively, glycerol, blank, the dl isomers of 2,3-butylene glycol, and blank.

The isolated glycols were transferred quantitatively to 100-ml volumetric flasks and diluted to the mark with water. The quantity of glycol present was determined by oxidizing two 25.00-ml aliquots by the recommended procedure[1]. It was found necessary, however, to dilute the samples obtained from the elution with 0.925*M* sodium borate with 25.00 ml of 50% sulfuric acid to prevent the precipitation of boric acid.

Calculations

The quantity of an isolated glycol in milligrams was calculated from the absorbance A, at 610 mμ, by use of the equation

$$\text{mg glycol} = \frac{A W_m}{10\, an} \times \text{dilution factor}$$

where W_m is the molecular weight of the glycol, n is the reduction capacity[1], and a is the absorptivity previously found[1] to be 0.1487. The dilution factor was 6.12 and 4.00, respectively for elutions with 0.925*M* sodium borate and 0.020*M* borax. The quantity of 1,2-propylene glycol was obtained from the equation

$$\text{mg 1,2-propylene glycol} = \left(\frac{A_1}{1.487} \times 6.12 - \frac{A_2}{1.487} \times 4.00 \right) \frac{W_m}{n}$$

where A_2 is the absorbance of the fraction which contained the isolated glycerol, and A_1 is the absorbance of the fraction which contained the mixture of 1,2-propylene glycol and glycerol. The quantity of the dl isomers of 2,3-butylene glycol was taken as the average value obtained from the two elutions.

RESULTS

The results shown in Table I were obtained by subjecting three known mixtures to analysis. Mixture 1 was analysed four times and the results were used to find the standard deviation, σ, for the determination of each glycol. Duplicate analyses were run on mixtures 2 and 3. Mean values for all mixtures were reported.

TABLE I

Glycol	Mixture 1 (55.90 mg) Taken mg	Found mg	σ	Mixt. 2 (25.27 mg) Taken mg	Found mg	Mixt. 3 (26.12 mg) Taken mg	Found mg
DEG	5.99	5.98	0.03	4.38	4.39	1.00	0.99
EG	8.33	8.60	0.24	0.61	0.59	13.88	13.86
PG	9.13	9.13	0.20	6.68	6.65	1.52	1.48
GL	8.95	8.71	0.07	6.65	6.38	1.49	1.50
BG, *m*	23.50	16.73	0.07	7.05	0.17	7.81	7.51
BG, dl		6.70	0.25		6.77	0.26	0.12

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A different source of 2,3-butylene glycol was used in each of the three analyses. Mixture 1 contained 2,3-butylene glycol from Du Pont and was found (Table I) to consist of 70.2% *meso* and 29.8% dl. The 2,3-butylene glycol in mixture 2, obtained from the National Research Council of Canada was found to be a mixture of 1.4% *meso* and 98.6% of the l isomer. The 2,3-butylene glycol from Celanese was previously chromatographed because of an oxidizable impurity which is eluted with glycerol with a 0.020*M* borax eluant and with the dl isomers of 2,3-butylene glycol in the elution with 0.925*M* sodium borate. Corrections for this impurity have been applied to the quantity found for glycerol and the dl isomers of 2,3-butylene glycol in mixture 3 of Table I.

DISCUSSION

With the exception of distillation, chromatographic procedures are the only known methods for the separation of glycol mixtures prior to analysis. The authors have reported the separation of diethylene glycol from dipropylene glycol[5] by a technique designated as salting-out chromatography. DAL NOGARE[6] employed partition chromatography for the separation of 1,2-propylene glycol, 2,3-butylene glycol, and 1,2-butylene glycol from ethylene glycol on silicic acid-celite columns. Fractions which contained the first three glycols were analysed by oxidation with periodate. In general, recoveries of 90 to 110% were found for 4 to 20 mg of each glycol determined.

In the method of analysis discussed in this paper, the time required for the elutions, when run simultaneously, was 10 hours. An analyst might prefer to decrease the flow rate of the longer elution (with 0.925*M* sodium borate eluant) from 0.5 to 0.3 cm per minute so that an overnight elution, which requires no attention, may be run. The fractions of effluent, collected with the aid of a fraction collector, could then be mixed and analysed.

It is not unusual for two batches of the same commercial resin to vary in both capacity and crosslinking. The batch of Dowex 1-X8 (lot No. 3902-30) used to obtain the foregoing data was found to differ appreciably from the resin that was used for the theoretical study of the elution behavior of the glycols[2] (lot No. 1196-24). For example, the concentration of sodium borate which was predicted to produce the separation described above was 0.75*M*. This was confirmed[3] by quantitative separations obtained with Dowex 1-X8, lot No. 3589-27, on a 50 cm × 2.28 sq. cm column. With this resin, the separation of the glycols was accomplished in 6 hours with a column height of 50 cm. Therefore, it is necessary that the elution characteristics of a given batch of resin be investigated in order that quantitative separations may be obtained.

Dowex 1 resins are subject to a slow decomposition in solutions of high pH. The exchange capacity is lowered by the formation of free amine from the quaternary-ammonium groups which serve as the exchange sites on the resin matrix. Over a period of one month, twenty elutions were run which required the passage of approximately 15 liters of 0.925*M* sodium borate. After this period, a redetermination of the elution graph of the mixture showed that the peaks were shifted toward the left. The differences between the peaks before and after this one-month period were found to be 3, 9, 13, 24, and 31 ml of effluent for DEG, EG, PG and GL, BG *m*, and

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BG dl,[1] respectively. The useful life of the resin may be extended by an increase in column height with periodic changes in the cut points. No decomposition was discernible for resin equilibrated with 0.020*M* borax over a period of 6 months.

SUMMARY

Procedures and results of the anion-exchange separation of diethylene glycol, ethylene glycol, 1,2-propylene glycol, the *meso* and the dl isomers of 2,3-butylene glycol, and glycerol are reported. This separation allows the determination of each of the six compounds present in the mixture by oxidation with dichromate.

RÉSUMÉ

Une méthode est décrite pour la séparation à l'aide d'une résine échangeuse d'anions de chaque constituant d'un mélange de diéthylèneglycol, éthylèneglycol, 1,2-propylèneglycol, *meso*-2,3-butylèneglycol, dl-2,3-butylèneglycol et glycérine. Le dosage de chaque glycol s'effectue après séparation par oxydation au moyen de dichromate.

ZUSAMMENFASSUNG

Nach der Trennung durch Anionenaustauschchromatographie eines Gemisches von Diäthylenglykol, Äthylenglykol, 1,2-Propylenglykol *meso*-2,3-Butandiol, dl-2,3-Butandiol und Glycerin, wird jedes Glykol durch Oxydation mit Dichromat bestimmt.

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Received July 16th, 1956

A RAPID COLORIMETRIC METHOD FOR THE DETERMINATION OF ALUMINIUM IN Cu-Al ALLOYS

by

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This method was developed for the analysis of aluminium brasses and bronzes. It was designed as a rapid routine method. The procedure described is for the 2% aluminium brasses, but slight modifications such as the aliquot taken for development of colour makes it applicable to the aluminium bronzes.

Procedure

Dissolve 1 g alloy in 10 ml nitric acid and dilute to 100 ml in a graduated flask. Pipette a 10 ml aliquot into a 100 ml beaker and add 5 ml sodium hydroxide solution. Boil 1 to 2 minutes, cool and dilute to 100 ml in a graduated flask. Allow the precipitate to settle (filter some of it if