The Determination of Pentaerythritol as the Dibenzylidene-acetal and its Chromatographic Separation from Commercial Material*

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The reaction of benzaldehyde with pentaerythritol to form the dibenzylidene-acetal is used as the basis of a method for the determination of pentaerythritol. A study has been made of the effects of formaldehyde, dipentaerythritol and liquid polyhydroxy compounds on the accuracy of the procedure and hence its applicability to liquors from the manufacturing process and to the commercial material. A chromatographic procedure has been developed for the separation of fairly pure pentaerythritol from impure samples; it is sufficiently pure to permit the use of the benzaldehyde procedure for its determination. This separation is based on the use of Celite adsorbent with acetone and acetone containing added water as solvents for extraction.

Pentaerythritol is a white solid, m.p.† 262° to 263° C, with four —CH_2OH groups spaced around a central carbon atom. It is widely used in the paint industry in the formation of alkyd resins. It is manufactured by the interaction of formaldehyde and acetaldehyde with lime or caustic soda, and because solid di- and poly-pentaerythritols and liquid polyhydroxy compounds can also be formed, the exact analysis of plant liquors and commercial

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† Determined by one of the authors (K. S.) on pentaerythritol made by hydrolysis of the dibenzylidene-acetal derivative that had been purified by repeated crystallisation from acetone.

products has always presented some difficulties. The most reliable procedure for the determination of pentaerythritol is based on the formation of the dibenzylidene-acetal complex with benzaldehyde,[1] but unfortunately, it is only applicable to fairly pure materials. A number of factors that affect this determination have been investigated in considerable detail. It has been shown that the presence of formaldehyde causes low results, whereas the presence of liquid hydroxy compounds and dipentaerythritol may cause high results. In these circumstances it was necessary to develop a separation procedure so that reasonably pure pentaerythritol could be isolated before the application of the benzaldehyde procedure.

Experiments showed that whereas the liquid hydroxy compounds were soluble in a number of organic solvents, pentaerythritol and dipentaerythritol were sparingly soluble. Pentaerythritol has a solubility in water of about 5 g per 100 ml at 20° C, whereas that of dipentaerythritol is about 0·2 g. With acetone and acetone containing 10 per cent. of water used, in turn, as solvents, a chromatographic method for the determination of pentaerythritol in reaction liquors and commercial products has been developed, Celite being used as the adsorbent. First, the liquid hydroxy compounds are extracted with acetone and then the pentaerythritol is extracted with the aqueous acetone. The pentaerythritol is determined in this second extract, after removal of the acetone, by the benzaldehyde procedure. The direct determination can, however, be made on commercial samples of pentaerythritol containing not more than about 2 per cent. of dipentaerythritol as impurity, but above this concentration the errors are significant.

Direct Benzaldehyde Condensation Procedure

Determination of pentaerythritol in commercial samples of pentaerythritol containing only dipentaerythritol as impurity

Experience in this laboratory indicates that probably the only reliable procedure for the determination of pentaerythritol is that based on the formation of its dibenzylidene-acetal derivative, which is a well-defined crystalline compound that melts at 159·5° C and is fairly insoluble in a dilute aqueous methanolic solution of hydrochloric acid containing benzaldehyde. The origin of the method is obscure, but the reaction was used by Kraft, who published[1] the results of a detailed investigation of the procedure. We have made extensive use of the method with only minor modifications involving closely controlled experimental conditions. When applied to the determination of the amount of pentaerythritol in commercial samples containing not more than about 2 per cent. of dipentaerythritol, which is the principal impurity in such samples, the procedure described below gave good results. Results for pure pentaerythritol and various samples containing a range of dipentaerythritol contents are shown in Table I. The effect of larger concentrations of dipentaerythritol is described on p. 32.

Table I

Determination of pentaerythritol by the benzaldehyde procedure

Weight of pentaerythritol taken, g	Weight of dipenterythritol taken, g	Dipentaerythritol in mixture, %	Pentaerythritol found (corrected), %
0·506	nil	nil	100·0
0·505	nil	nil	99·9
0·499	0·005	1	100·0
0·499	0·010	2	100·1
0·501	0·021	4	101·3

Method

Reagents—

Benzaldehyde reagent—One part of freshly distilled benzaldehyde or fresh AnalaR material mixed with 5 parts of anhydrous methanol.

Hydrochloric acid, concentrated.

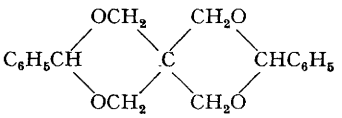
Wash solution—One part of methanol mixed with 1 part of water, the mixture being maintained at 0° C.

PROCEDURE—

A known weight (0·4 to 0·7 g) of the sample was dissolved in 15 ml of water in a 100-ml conical flask by warming. The solution was heated to boiling, 15 ml of the benzaldehyde reagent were then added and the contents of the flask were mixed by swirling. Next, 12 ml of concentrated hydrochloric acid were added immediately and the flask was again swirled for 5 minutes. The flask was stoppered with a ground-glass stopper and shaken occasionally until cool; it was then set aside at room temperature overnight. After cooling in a bath of ice for 1 hour, the reaction mixture was diluted with 25 ml of ice-cold wash solution, mixed thoroughly and then filtered through a tared sintered-glass crucible (porosity grade No. 1, 2 or 3; previously dried at 110° C) in which was placed a short glass rod to aid filtration. Any residual precipitate was easily washed from the flask by swirling with the ice-cold wash solution, a total of about 100 ml being used. The crucible was dried to constant weight at 100° to 110° C.

As the dibenzylidene-acetal derivative of pentaerythritol was slightly soluble in the wash solution, it was necessary to apply a correction to the weight of precipitate found. This solubility was 0·0135 g under the conditions used, and it was determined by performing the procedure on a sample of pure pentaerythritol. From a knowledge of the weight of pentaerythritol taken and the amount of dibenzylidene-acetal derivative found, the amount of pentaerythritol lost in the reaction was determined.

The formula for dibenzylidenepentaerythritol is—



and pentaerythritol, % w/w $= \dfrac{(\text{weight of precipitate, g} + 0{\cdot}0135\text{ g}) \times 0{\cdot}436 \times 100}{\text{weight of sample, g}}$.

FACTORS THAT AFFECT THE BENZALDEHYDE PROCEDURE

A number of factors that were considered to have some effect on the dibenzylidene-acetal method were studied in relation to the possible use of the procedure for the determination of pentaerythritol in impure materials and those derived from plant processes. These factors included the effect of formaldehyde, dipentaerythritol and liquid hydroxy impurities, all of which may be present in plant reaction liquors. A more detailed examination of the effect of high concentrations of dipentaerythritol was required, because of its possible presence in large amounts in commercial samples of pentaerythritol.

Of the reagents used in the benzaldehyde procedure, it was found that the only reagent requiring careful attention was the benzaldehyde. It was essential to ensure that only redistilled material was used, or preferably AnalaR material. The results were poorer with impure benzaldehyde, probably owing to the presence of benzoic acid.

EFFECT OF FORMALDEHYDE—

Determinations of pentaerythritol were made on mixtures of pure pentaerythritol and formaldehyde by the method described above. The results for different pentaerythritol - formaldehyde mixtures are shown in Table II.

TABLE II

DETERMINATION OF PENTAERYTHRITOL BY THE BENZALDEHYDE CONDENSATION REACTION: EFFECT OF FORMALDEHYDE

Pentaerythritol taken, g	Formaldehyde added, g	Pentaerythritol found, % of original	Remarks
0·510	None	98·0	Slow precipitation of the complex in the presence of formaldehyde
0·496	0·4	80·5	
0·517	1·2	43·1	
0·553	2·0	19·2	

The results indicate the marked effect of the presence of formaldehyde in causing low results for the determination of pentaerythritol. In reaction liquors the effect of formaldehyde alone is such that the value found for pentaerythritol might be less than 80 per cent. of the amount present.

EFFECT OF DIPENTAERYTHRITOL—

Table I shows that quantities of dipentaerythritol up to about 2 per cent. of the pentaerythritol present do not appreciably affect the result for pentaerythritol. It was not known whether plant liquors would contain more than 2 per cent. of dipentaerythritol, and it was considered possible that such samples of pentaerythritol might be encountered in practice. Further experiments were made in order to discover the influence of larger amounts of dipentaerythritol (more than 4 per cent.) on the benzaldehyde method and the results of these experiments are shown in Table III. These results show that the errors in the determination of pentaerythritol increase as the amount of dipentaerythritol in the sample is progressively increased.

TABLE III

DETERMINATION OF PENTAERYTHRITOL BY THE BENZALDEHYDE CONDENSATION REACTION: EFFECT OF DIPENTAERYTHRITOL

Mixture				
Pentaerythritol, g	Dipentaerythritol, g	Dipentaerythritol in mixture, %	Pentaerythritol found, %	Remarks
0·537	0·022	4	101·6	
0·482	0·046	9	101·8	
0·506	0·074	13	102·5	
0·492	0·088	15	104·5	
0·500	0·147	22	109·0	
0·655	0·193	23	111·0	Precipitate visibly contaminated with oily dipentaerythritol derivative
0·629	0·371	37	128·0	
0·547	0·697	56	137·0	
0·545	0·698	56	160·0	

Dipentaerythritol reacts with benzaldehyde to form an oily product that may be incompletely removed by the wash liquor and so cause high results for pentaerythritol.

EFFECT OF LIQUID HYDROXY COMPOUNDS—

The liquors derived from the plant process in the manufacture of pentaerythritol may contain impurities that exist as a syrup when separated from the aqueous solution. The exact nature of these compounds is not known, but preliminary experiments have shown that they contain hydroxyl groups and loosely bound formaldehyde groups. These compounds seriously interfere with the benzaldehyde procedure for the determination of pentaerythritol, as they cause high results. Like dipentaerythritol, they form an oily product that cannot be completely removed from the crystalline pentaerythritol derivative by washing. As will be seen later, they can be separated from pentaerythritol and dipentaerythritol by making use of their solubility in acetone. Whereas there does not appear to be any direct chemical method for the determination of small amounts of dipentaerythritol in fairly pure pentaerythritol, small amounts of these syrupy impurities can be determined colorimetrically with chromotropic acid, with which their formaldehyde linkage apparently reacts.[2]

The results for the determination of pentaerythritol in mixtures containing syrupy hydroxy compounds by the benzaldehyde condensation procedure are shown in Table IV. A supply of these compounds was produced by extracting them with dry acetone from samples of "purge" liquor (a waste plant material containing large amounts of these compounds) that had been submitted to a chromatographic separation.

The acetone was removed from the extracts of the hydroxy compounds, and the syrup was dried in a desiccator under reduced pressure; there was no appreciable loss due to volatility. The results show the error in the determination of pentaerythritol by the benzaldehyde method with increasing amounts of the impurities.

TABLE IV

DETERMINATION OF PENTAERYTHRITOL BY THE BENZALDEHYDE CONDENSATION REACTION: EFFECT OF LIQUID HYDROXY COMPOUNDS

Mixture				
Pentaerythritol, g	Liquid hydroxy compounds, g	Liquid hydroxy compounds, %	Pentaerythritol found, g	Recovery,* %
0·506	0·132	21	0·528	104
0·584	0·173	23	0·617	106
0·632	0·323	34	0·695	110
0·596	0·430	42	0·633	106
0·584	1·096	65	0·714	122
0·654	1·497	70	0·933	143
0·452	2·008	82	0·802	177
0·626	3·020	83	1·060	170

No higher values of recovery were found owing to complete exhaustion of the benzaldehyde reagent.
* All precipitates were very crude.

DISCUSSION OF THE DIBENZYLIDENE-ACETAL PROCEDURE—

It has been shown that the benzaldehyde condensation procedure cannot be used for the direct determination of pentaerythritol in plant liquors or unknown commercial products that might contain more than 2 per cent. of dipentaerythritol. The presence of formaldehyde in liquors causes low results and the presence of liquid hydroxy impurities cause high values for pentaerythritol. Although the effect of formaldehyde could be removed by steam-distillation of the liquor, the difficulty due to the other impurities is not readily overcome.

Preliminary experiments on synthetic mixtures of pentaerythritol, dipentaerythritol and liquid impurities showed that it might be possible to find solvents that could be used in conjunction with a chromatographic method for the separation of pentaerythritol in a sufficient degree of purity to be suitable for determination by the benzaldehyde condensation procedure. Further work was done with this aim in view.

Chromatographic Procedure

PRELIMINARY STUDY OF THE SOLUBILITY OF PENTAERYTHRITOL, DIPENTAERYTHRITOL AND LIQUID IMPURITIES IN VARIOUS SOLVENTS—

In order to develop a chromatographic procedure for the separation of the pentaerythritol, it was necessary to choose a suitable solvent. Approximate determinations of the solubilities of pentaerythritol and dipentaerythritol in a number of common solvents were therefore made. The solubilities were determined by stirring an excess of the solid with the appropriate solvent. After sufficient time had been allowed for saturation, the solvent was separated from the solid, the solution was evaporated to dryness and the residue was weighed. The results for a number of solvents at various temperatures are shown in Table V.

TABLE V

SOLUBILITY OF PENTAERYTHRITOL AND DIPENTAERYTHRITOL IN VARIOUS SOLVENTS

Solvent	Solubility	
	Pentaerythritol, g per 100 ml	Dipentaerythritol, g per 100 ml
Water	5·983 (21·5° C)	0·197 (24° C)
Pyridine	1·229 (20° C)	0·052 (24·5° C)
Methanol	0·485 (20° C)	0·024 (27·5° C)
Butanol	0·105 (28·5° C)	0·014 (28·5° C)
*iso*Propanol	0·050 (25° C)	0·012 (27·5° C)
Acetone	0·021 (22° C)	nil
Ethyl methyl ketone	0·011 (24·5° C)	nil
Ether	nil	nil
Chloroform	nil	nil
Benzene	nil	nil

These results show that of the solvents examined the best for pentaerythritol is water. The solubility of dipentaerythritol in water is small. The liquid impurities were found to be soluble in water and in acetone. The results show that the solubility of pentaerythritol in a number of organic solvents including acetone is very small; similarly for dipentaerythritol. It was considered that if a suitable adsorbent could be found and used in conjunction with acetone and acetone - water mixtures, it might be possible to separate the pentaerythritol from the liquid impurities chromatographically in a sufficiently pure state to permit the determination of pentaerythritol to be completed by the benzaldehyde procedure.

CHOICE OF ADSORBENT FOR USE IN THE CHROMATOGRAPHIC SEPARATION OF PENTAERYTHRITOL WITH ACETONE AND ACETONE - WATER MIXTURES—

In view of the results of the solubility determinations, it was considered that attempts should be first made to separate liquid impurities from a suitable adsorbent by means of acetone and to follow this with a further extraction with acetone containing water in order to extract pentaerythritol. From the results shown in Table V it did not seem to be practicable to separate pentaerythritol directly by one extraction without also extracting the liquid impurities.

Experiments showed that under fairly dry conditions a large proportion of liquid impurities could be extracted chromatographically from a sample without appreciable extraction of pentaerythritol. If the solvent was then changed to acetone containing 10 per cent. v/v of water, pentaerythritol could be quantitatively extracted with only slight extraction of the remaining impurities, the impurities extracted being insufficient to interfere with the benzaldehyde procedure used for the final determination of pentaerythritol. Preliminary experiments involved a search for suitable adsorbent for use in conjunction with the solvents. Both alumina and cellulose proved too retentive for both the liquid impurities and pentaerythritol, but Celite was found to be a suitable adsorbent.

METHOD

REAGENTS—

Celite No. 535 for chromatography.

Acetone, pure grade (less than 0·3 per cent. of water)—Specific gravity should not exceed 0·787 at 15·5° C/15·5° C.

Solvent mixture—900 ml of acetone mixed with 100 ml of water.

Benzaldehyde reagent—One part of freshly distilled benzaldehyde or fresh AnalaR material mixed with 5 parts of anhydrous methanol.

Hydrochloric acid, concentrated.

Wash solution—One part of methanol mixed with 1 part of water, the mixture being maintained at 0° C.

PREPARATION OF COLUMN—

The tube used for the chromatographic extraction was 1·8 to 2·0 cm in diameter and 28 cm long with a funnel at its top to facilitate introduction of the sample into the column. It terminated in a short length of glass tubing (6 mm in diameter) and was made water-repellent by applying silicone treatment before use.

About 5 g of Celite No. 535 were weighed into a 250-ml beaker and slurried with about 50 ml of acetone. The mixture was poured into the chromatograph tube at the base of which a small piece of cotton-wool had been placed. A further 50 ml of acetone were used for washing the beaker. These washings were poured into the column and the solvent was allowed to drain to the level of the Celite. The outlet of the column was closed with a small rubber stopper.

PREPARATION OF THE SAMPLE—

Sufficient sample was weighed into a 150-ml beaker to provide preferably about 0·4 to 0·7 g of pentaerythritol, although smaller amounts were used. For plant liquors the sample was evaporated to 5 ml and then heated just to boiling and 5 g of Celite No. 535 were added. The mixture was thoroughly stirred with a stout glass rod and then heated in the beaker at 100° C for 1 hour. The sample was placed in a desiccator and kept under reduced pressure for 30 minutes.

When analyses were required on solid samples, 5 ml of water were added to an appropriate weight of sample and after addition of Celite the above procedure was followed. Complete solution of the sample in water was not always possible, as it depended on the amount of dipentaerythritol present.

EXTRACTION AND DETERMINATION OF PENTAERYTHRITOL—

The contents of the 150-ml beaker were well mixed with 10 ml of acetone with the aid of a stout glass rod. The mixture was transferred to the top of the prepared column, the beaker was washed three times with 10-ml quantities of acetone and the eluate was collected in the original beaker. The column was washed twice with 20-ml portions of acetone, each time the solvent being allowed to drain to the level of the Celite. The beaker containing the liquid hydroxy compounds was replaced by a 500-ml conical flask and the column was then extracted with 350 ml of acetone containing 10 per cent. of water. This acetone - water extract containing the pentaerythritol was evaporated to 50 ml on a steam-bath and the residual solution was then transferred to a 100-ml conical flask fitted with a ground-glass neck. The evaporation on the steam-bath was continued until the volume of the solution was reduced to about 15 ml. Pentaerythritol was then determined by precipitation of the dibenzylidene-acetal derivative as described on p. 30. In the calculation of the result of the determination it was necessary to add 10 mg to the amount of pentaerythritol found. This represented the solubility of pentaerythritol in the dry acetone used as solvent in the first extraction for the removal of liquid impurities. It would be necessary to perform this blank determination on any particular batch of acetone that might not be completely free from water.

RESULTS

DETERMINATION OF PENTAERYTHRITOL WITH IMPURITIES ABSENT—

The results shown in Table VI were found for aqueous solutions containing known amounts of pentaerythritol by the full chromatographic procedure described on p. 34. They show excellent recoveries for pentaerythritol after adding 10 mg (representing the solubility of pentaerythritol in dry acetone) to the amount determined in the acetone - water solvent.

TABLE VI

CHROMATOGRAPHIC SEPARATION OF PENTAERYTHRITOL ON CELITE ADSORBENT

Pentaerythritol taken, g	Weight of pentaerythritol found in acetone extract, g	Weight of pentaerythritol found in acetone - water extract by benzaldehyde condensation method, g	Total pentaerythritol found with 10-mg correction, g
0·340	0·011	0·329	0·339
0·396	0·014	0·383	0·393
0·399	0·010	0·387	0·397
0·463	0·010	0·454	0·464
0·502	0·010	0·493	0·503
0·702	0·011	0·689	0·699

EFFECT OF LIQUID IMPURITIES—

Table VII shows the amounts of liquid impurities extracted by the two solvents in the chromatographic procedure. The liquid impurities used in these experiments were obtained

TABLE VII

CHROMATOGRAPHIC SEPARATION OF LIQUID IMPURITIES ON CELITE ADSORBENT

Liquid impurities taken, g	Weight of liquid impurities found in acetone extract, g	Weight of liquid impurities found in acetone - water extract, g	Liquid impurities recovered (total), g
0·503	0·438	0·044	0·482
1·024	0·940	0·054	0·994

from plant purge liquor by means of the chromatographic procedure described on p. 34. The results show that the liquid impurities are not extracted quantitatively by the dry acetone and that a further portion is extracted by the acetone - water. However, it will be seen from Table VIII that there is no appreciable interference by these residual liquid impurities with the determination of pentaerythritol.

TABLE VIII

CHROMATOGRAPHIC SEPARATION OF PENTAERYTHRITOL AND LIQUID IMPURITIES FROM MIXTURES CONTAINING BOTH SUBSTANCES

Mixture		Weight of liquid impurities found in acetone extract, g	Weight of pentaerythritol found in acetone - water extract (by benzaldehyde condensation method), g	Pentaerythritol found (with +10 mg correction), g
Pentaerythritol, g	Liquid impurities, g			
0·595	0·089	0·069	0·582	0·592
0·593	0·100	0·063	0·589	0·599
0·561	0·174	0·131	0·559	0·569
0·754	0·540	0·403	0·756	0·766
0·641	0·546	0·385	0·650	0·660
0·606	0·659	0·490	0·618	0·628

EFFECT OF DIPENTAERYTHRITOL—

Because commercial pentaerythritol might contain high concentrations of dipentaerythritol, a number of analyses of pentaerythritol - dipentaerythritol mixtures were made by the chromatographic separation - benzaldehyde condensation procedure. As the solubility of dipentaerythritol in water is small compared with that of pentaerythritol (see Table V), the sample did not always dissolve in water before absorption on Celite. Results for mixtures of pentaerythritol and dipentaerythritol are shown in Table IX. They show that even with mixtures containing more dipentaerythritol than pentaerythritol, the results are good.

TABLE IX

CHROMATOGRAPHIC SEPARATION AND DETERMINATION OF PENTAERYTHRITOL IN MIXTURES CONTAINING DIPENTAERYTHRITOL

Mixture taken		Amount of pentaerythritol (+10 mg correction) found, g
Pentaerythritol, g	Dipentaerythritol, g	
0·421	0·281	0·431
0·406	0·607	0·398
0·467	0·901	0·469
0·460	nil	0·459

CONCLUSIONS

Factors affecting the benzaldehyde procedure for the determination of pentaerythritol have been examined and it has been shown that the procedure cannot be applied directly to commercial samples of unknown purity or to liquors from the manufacturing process. A chromatographic method is described for the separation of pentaerythritol before the application of the benzaldehyde procedure. It is applicable to commercial samples and liquors.

REFERENCES

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