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Note

Gas chromatographic determination of water in acetone

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In a study designed to develop a continuous process[1] for obtaining a cocoa butter-like fraction from beef tallow by acetone fractionation, the water content in the acetone was critical[2]. Therefore, monitoring the water content of acetone used in all stages of this experimental process was necessary. A quantitative method was required that was both rapid and reliable.

The standard Karl Fischer titration for determining water was not suitable because of ketonic interference. Even an alternate procedure of substituting freshly distilled pyridine for methanol as the solvent permitted only the approximate determination of small amounts of water in carbonyl compounds[3].

Other methods reported in the literature for determining water in liquids utilize gas chromatographic (GC) separation with thermal conductivity detection. Smith[4], probably one of the earliest researchers to publish GC data on the quantitative determination of water in an organic system, used three methods of quantitation, namely: internal normalization, calibrated standard curve, and an internal standard method. Bennet[5], in a further study of GC separation of aqueous organic solutions, measured peak height and interpreted the percent water from a corresponding calibration curve. However, because of possible changes in the column or detector, the calibration curve had to be reestablished periodically. Hogan *et al.*[6] used an internal standard technique employing methanol as the standard to eliminate the need for daily area calibrations. A shortcoming of this procedure was the necessity to measure the water content of the internal standard prior to addition to the samples.

MacDonald and Brady[7] combined the method of standard addition with gas chromatography to yield a technique that was superior to those previously available. However, when we employed this method in our study, we encountered difficulties. For example, water peaks were not reproducible because of moderate tailing, thus resulting in poor quantitation.

We modified MacDonald and Brady's method to permit analysis of a wider range of water contents (0.2–4.0%) in acetone. The changes include column packing, method of sample preparation, adjustment of sample size, and the use of a Chaney adaptor to insure injection of a constant volume of sample.

EXPERIMENTAL*

Apparatus

A Varian Aerograph chromatograph Model 1520 C with thermal conductivity detector (TCD) set at 200°C and 125 mA was used. The separating column was 6 ft. × 1/8 in. stainless steel packed with Chromosorb 102 (Johns-Manville), 80–100 mesh. Operating conditions were as follows: column, 150°C; injection port, 175°C; helium carrier gas flow-rate, 40 ml/min; sample size, 0.5 μl. An Infotronics Model CRS 100 integrator with automatic attenuation set at × 10 was used to integrate all peak areas.

Procedure

Sample preparation by the method of standard addition was as follows. Approximately 20.0 g of acetone was weighed into a tared 25-ml volumetric flask fitted with snap-cap closure. To this, varying weights of water (100 to 300 mg) were added with a weighing buret, and the solution was thoroughly mixed. In general, at least two separate weights of water were added to each acetone sample.

Initially, 0.5 μl of "neat" acetone was injected into the chromatograph with a 1.0-μl Hamilton syringe fitted with a Chaney adaptor. The retention time and area of the water peak were measured. Then, 0.5 μl of "addition" solution was injected, and the new area of the water peak was determined. Injections were repeated in this manner a minimum of four times, and the mean area value of the water peak was calculated. These values were used in calculating the weight of water in acetone.

Calculation

The weight percent of water in acetone was calculated by the following rearrangement of MacDonald and Brady's equation[7]:

$$M = \frac{(W_a \times A_a) \times (W_s - W_a)}{(W_s \times A_s) - (W_a \times A_a)}$$

where

M = weight of water in acetone
W_a = weight of acetone before standard addition
W_s = weight of acetone after standard addition
A_a = mean area of water peak before standard addition
A_s = mean area of water peak after standard addition

When M and W_a are known, the water content (%, w/w) = $(M/W_a) \times 100\%$

RESULTS AND DISCUSSION

Initially, Chromosorb 104 (an acrylonitrile–divinylbenzene polymer) was used as recommended by MacDonald and Brady. Moderate tailing of the water peak resulted in poor quantitation.

* Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

Peak tailing is indicative of hydrogen bonding of water to the solid support of the column packing or to the column tubing itself. Tailing also may be caused by an overload of the thermal conductivity detector due to injection of excess sample volume. All three conditions will result in poor peak area reproducibility, thereby affecting the accuracy and precision of the method.

To minimize the adsorption effects, the stainless steel column was silanized before being packed. It has also been reported that inert porous polymer packings, such as the Chromosorb Century Series, have unique selectivities which depend on the functional groups chemically bound to the cross-linked polymer[8]. For example, Chromosorb 104 appears to be more suited for separating trace amounts of water (0.1%) as demonstrated by MacDonald and Brady, whereas Chromosorb 102 (a styrene–divinylbenzene polymer) is more efficient for separating of higher concentrations of water (4.0%) in acetone. For this reason, Chromosorb 102 was used in the present study. Because of the wide range (0.20–4.0%) of water concentrations encountered it was observed that a 10-μl sample, as recommended by MacDonald and Brady, caused a TCD overload as manifested by a slow return of the pen to baseline. A study of the effect of sample volume indicated that a 0.5-μl aliquot gave a satisfactory separation of the two peaks (Fig. 1) and a consistent retention time for the water peak over the range of concentrations encountered. The method was further refined by the use of a 1.0-μl Hamilton syringe fitted with a Chaney adaptor and the technique of direct on-column injection of the sample.

These refinements permitted several grades of acetone as well as acetone cuts from various stages of the continuous extraction procedure to be analyzed. Table I includes quantitative data from three types of samples representative of all analyses made in this study.

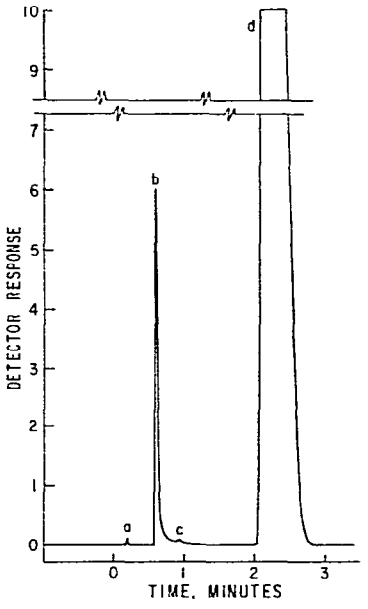

Fig. 1. Typical chromatogram showing the separation of a 2% water in acetone solution. Peaks: a = air; b = water; c = impurity; d = acetone.

TABLE I

EXPERIMENTAL DATA AND ANALYTICAL RESULTS OF ACETONE ANALYSES

Sample	*Water added (g)*	*n*	*Area of water peaks (mV sec)*		*Water content (%)*	*C.V. (%)*
			Neat	*After addition*		
ACS-grade	0.20707	5	4707	26,510	0.219	2.58
acetone	0.20186	5	4707	25,136	0.226	0.94
Feed	0.20109	5	12,883	15,716	4.19	2.01
acetone	0.28471	4	12,883	17,316	3.92	1.20
Recycled	0.18827	6	13,876	18,587	2.41	4.08
acetone	0.10672	4	13,279	16,197	2.35	3.94

The first sample was the ACS- or reagent-grade acetone which had been used in the start-up of the continuous process for extraction of animal fats. It had an average mean area for the water peak of "neat" acetone of 4707 mV sec with an average standard deviation of 105 mV sec. After two separate additions of water to this acetone, the water peak areas averaged 26,510 and 25,136 mV sec with standard deviations between replicates of 583 and 195 mV sec, respectively. The water concentration of this sample as determined by the method of standard addition and calculated by the formula previously presented averaged 0.223%, having standard deviations of 0.006 and 0.002, respectively, for the two weights. The coefficient of variation (C.V.) averaged 1.75%.

The second sample, identified as feed acetone, also had been used in the experimental tallow fractionation pilot plant study. This sample came from the evaporator used to recover acetone from the fat for recycling. (The acetone must be dried before being recycled to the process.) A sample of this acetone was analyzed for water content. It had an average peak area of 12,883 mV sec for "neat" acetone with a standard deviation of 38 mV sec between replicates. Area counts of 15,716 and 17,316 mV sec were obtained after two separate additions of water to the feed acetone. The standard deviations of these data were 61 and 58 mV sec, and the calculated water content averaged 4.19 and 3.92%, respectively. The standard deviations of these data were 0.08 and 0.05, respectively, with an average C.V. of 1.60%.

The third sample shown is a recycled acetone, also from the tallow fractionation studies. This acetone, recovered from the evaporator, was partially dried by being passed through molecular sieves prior to GC analysis. The sample had averaged peak areas for "neat" acetone of 13,876 and 13,279 mV sec with standard deviations of 214 and 45 mV sec for 6 and 4 replicates, respectively. After two separate additions of water the area water peaks averaged 18,587 and 16,197 mV sec, respectively, with standard deviations of 195 and 120 mV sec. These data were used to calculate average water contents of 2.41 and 2.35% water with standard deviations of 0.1 and 0.09, equivalent to a C.V. of 3.99%.

This study has demonstrated the feasibility of using the method of standard addition for determining water in acetone up to a concentration of at least 4.0%.

Results of this work also show that concentrations of water as low as 0.2% can be determined accurately. Of the adsorbent systems tried, the Century Series Chromosorb 102 gave satisfactory separation of water and acetone and reproducible areas of the water peak. Finally, we found that overloading of the TCD could be avoided by limiting the sample volume to 0.5 μl, precisely measured each time with a Chaney adaptor.

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