6A, 68, 6C) suggesting possible orientations of the entire point bar within the ancient river channel. Study of their models leads to the idea that migrating point bars may assume almost any orientation within the channel. Also, their models depict point bars exhibiting various degrees of curvature in their external morphology. It is important to realize that this curvature is commonplace in the growth of a point bar; that the bar is sinuous throughout its length; and that the sinuosity of the point bar is an expression of the range of orientations of its component dunes.

The exposures studied doubtless represent random cuts through a lithified point bar. There is no way of knowing the entire dimension or morphology of the point bar from the present exposures. Nor is the orientation of the present exposures known with respect to overall form or morphology of the ancient point bar. Therefore, it is hazardous to predict regional stream flow trends on the basis of trends indicated in partial exposures, particularly on a point bar.

The proposal of Beutner, et al., that the point bar migrated westward may or may not be correct. One possible alternative is that the exposed sandstone complex may represent a portion of an ancient point bar that is oriented approximately parallel to, rather than perpendicular to, the bounding river banks. In such a case, the apparent migration could be misleading.

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LITERATURE CITED

Allen, J. R. L., 1965, "The Sedimentation and Paleogeography of the Old Red Sandstone of Anglesey, North Wales", *Yorkshire Geol. Soc. Proc.*, v. 35, p. 152.

Bagnold, R. A., 1956, "The Flow of Cohesionless Grains in Fluids", *Roy. Soc. London Phil. Trans.*, ser. A, no. 964, v. 249, p. 235-297.

Beutner, Flueckinger, and Gard, 1967, "Bedding Geometry in a Pennsylvanian Channel Sandstone", *Geological Society of America Bulletin*, v. 78, p. 911-916.

Brett, G. W., 1955, "Cross-Bedding in the Baraboo Quartzite of Wisconsin", *Journal of Geology*, v. 63, p. 143-148.

Harms, J. C. and Fahnstock, R. K., 1965, "Stratification, Bed Forms and Flow Phenomena (with an example from the Rio Grande)", *Society of Economic Paleontologists and Mineralogists Special Publication*, no. 12, p. 84-115.

Leopold, Luna B., 1964, *Fluvial Processes in Geomorphology*, W. H. Freeman and Company, p. 200-223.

Leopold, Luna B. and Langbein, W. B., 1966, "River Meanders", *Scientific American*, v. 214, no. 6, p. 60-70.

Potter, P. E. and Pettijohn, F. J., 1963, *Paleocurrents and Basin Analysis*, Academic Press, Inc.

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THE QUALITATIVE AND QUANTITATIVE DETERMINATION OF THE ESTERS BY ALKALINE HYDROLYSIS AND GAS CHROMATOGRAPHIC ANALYSIS OF THE LIBERATED ALCOHOL

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ABSTRACT

A procedure for the qualitative and quantitative analysis of some volatile and non-volatile esters by alkaline hydrolysis and gas chromatographic analysis of the liberated alcohol is described and evaluated. Samples of approximately 10-50 mg. in size were processed with an easily obtainable accuracy of 99 plus per cent. Conditions are described which conveniently allow complete retention of the volatile alcohols prior to and during the sample injection. Since the procedure presents no special difficulties for esters of the higher alcohols, considerable data is presented only for some methyl and ethyl esters.

INTRODUCTION

The qualitative and quantitative analysis of volatile esters by the methods of gas-liquid chromatopraphy is standard procedure.[1,2] This procedure merely compares the response of the unknown sample and internal standard with that of a similar reference sample. However, with the increasing complexity of the samples analyzed by gas chromatography, additional quantitative gas chromatographic data other than just the response of the compound in question is most helpful, especially for samples of unknown composition.

EXPERIMENTAL

Apparatus: A Barber-Colman Gas Chromatograph equipped with a flame ionization detector and strip chart recorder was employed in this investigation. The column used as a 6 ft. by ¼ in. o.d. coiled glass packed with 10% Carbowax 4000 on 100/120 Anakrom ABS. Nitrogen was employed as the carrier gas. Sample injections were made with a 5 microliter Hamilton Syringe. Quantitative Procedures: An accurately measured quantity of approximately 10-25 mg of the esters was weighed into one-half ounce screw-cap bottles. A predetermined amount of n-butyl-p-aminobenzoate was

added as a marker. To this mixture was added 1.5-2 ml. of propylene glycol. The mixture was then warmed (non-volatile esters were present) to hasten solution and 1.5-2 ml. of distilled water added (or the water was added to the appearance of a turbidity); the solution was then cooled, 2-3 drops of 30% sodium hydroxide solution were added and the bottle was immediately capped and tightened with pliers or some other suitable aid. The sample was then mixed and placed in a 37°C. water bath for 24 hours. Esters containing functional groups which tend to retard the rate of alkaline hydrolysis required 36-48 hours for complete hydrolysis.

After complete hydrolysis had taken place, the sample was cooled to approximately 0°C. and maintained at this temperature for approximately 30 minutes. The sample was then removed from the ice bath, immediately transferred to a cold test tube, and centrifuged to separate the solution from any solid matter that was present. Injections of this cold solution were then made into the gas chromatograph. In order to obtain quantitative results, the sample must remain chilled during all operations prior to injection. In addition considerable experience has shown that the column head may rapidly accumulate considerable debris and should be occasionally replaced with a fresh section of column material.[3]

Samples containing extremely low concentrations of non-volatile and extractable esters were extracted with the appropriate solvent and concentrated by evaporation. The residue was then quantitatively transferred to the one-half ounce bottle and the volatiles were completely removed by vacuum techniques or gentle evaporation.

Reference And Standard Solutions: Reference methyl nicotinate was employed as a standard for the determination of methyl esters and for alcohol retention studies. A sample approximately equivalent in alcohol content to the unknown was processed as described in the Quantitative Procedure with each unknown. An additional methyl nicotinate sample was weighed into the one-half ounce bottle and dissolved in 1.5-2 ml. of water. An accurately measured quantity (pre-determined to produce a satisfactory response) of n-butyl alcohol was added and the mixture was cooled to about 0°C. Two or three drops of cold 30% sodium hydroxide were then added and the cap securely tightened. This standard was then placed at 0°C. for 24 hours and processed with the unknown. The low temperature employed for the hydrolysis presented no difficulties since methyl nicotinate under these conditions is 100% hydrolyzed.

Reference ethyl-p-aminoberzoate was employed as the standard for the determination of ethyl esters. A sample approximately equivalent in alcohol content to the unknown was processed as described in the Quantitative Procedure with each unknown.

As an additional check, standard solutions of methanol and ethanol were prepared immediately prior to injection of the unknown.

Qualitative Analysis: Qualitative analysis was done quite conveniently and with very little loss of time. The sample was injected immediately after the addition of the 30% sodium hydroxide solution. Studies have shown-see Table I-that about 40-50% hydrolysis, which is quite adequate for purposes of identification, takes place upon injection.

Analysis Data and Results

TABLE I: *Qualitative Analysis*

Conditions: Column-10% Carbowax 4000 on 100/120 Aana-ABS
Column temperature-100•C. (70-80•C. for methanol in the presence of excess ethanol)
Flash Heater temperature-230°C (Essentially by-passed with 2 in. needle)
Detector-200° C. Nitrogen-60 ml/min.
Injection- 3-4 microliters

Compound	*Quantity Hydrolyzed*
Yohimbine HC1	>50%
Methyl nicotinate	>50%
Ethyl-p-aminobenzoate	40-50%
Methyl salicylate	>50%
Chlorophyll[4,5]	methyl ester present

TABLE II. *Quantitative Analysis*

Conditions: as in TABLE I

Compound	*Amount Present* (mg.)	*Amount Found %*
Methyl salicylate	37.4	98.0
	39.7	98.8
Yohimbine HC1	53.2	97.0
	67.1	102.5
	0.9-1.1	104.0 (*)
Methyl-p-hydroxy-benzoate	2.25-2.75	105.1 (*)
Diethyl phtalate	35.1	102.4
	29.2	102.5
	2.56 (by G. C. of ester)	100.0
	2.26-2.74	105.1 (*)
Butyl-p-amino-benzoate	25-35	Quantitative

(*) calculated from mean
Total No. Determinations: 24 (not all shown)
Recovery Range: 95-107% without marker, 97-102.5% with marker (uncorrected for sample purity)
Sample Purity: 99-101% or conforms to the United States Pharmacopeia.

Literature Cited

1. The National Formulary XIII. 779 p.
2. Kuelemans, A.I.M. 1959. Gas Chromatography. Reinhold Publishing Corporation, New York. 18p.
3. Garavelli, C. B. 1960-62. Progress Report. University of Tennessee, Memphis, Tennessee.
4. Molisch. 1896. Ber. botan. Ges. 14:16.
5. Official Methods Of Analysis Of The Association Of Official Agricultural Chemists. Ninth Edition: 92,579p.