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HIGH-RESOLUTION SUBTRACTIVE GAS CHROMATOGRAPHY

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SUMMARY

The subtraction of carboxylic acids by high-resolution gas chromatography with a microreactor, filled with zinc oxide is described. Application to the subtraction of organic acids is documented.

INTRODUCTION

Subtractive gas chromatography is a rapid method for organic functional group analysis. The subtraction of compounds is obtained by reaction, in the gas chromatographic (GC) system, with a specific reagent that selectively retains these compounds with the formation of non-volatile derivatives. By comparing chromatograms obtained with and without these reagents the evaluation of compounds with a particular functional group is possible and can serve as a useful aid in the GC analysis of complex mixtures. Examples of subtractive systems for compounds containing various functional groups have been reported[1–5].

The present report describes the subtraction of free carboxylic acids with a simple microreactor, a glass tube, filled with zinc oxide and placed in the injection port.

EXPERIMENTAL

A Carlo Erba 4160 gas chromatograph with automatic split–splitless injection and a flame ionization detector was employed. The carrier gas was nitrogen at 2 ml/min. The column was a 15-m glass capillary containing OV-1701. Temperature program: 6 min at 80°C; then to 130°C at 5°C/min; 3 min at 130°C; then to 160°C at 3°C/min and finally held for 20 min. The microreactor comprised a glass tube, 60 × 4 mm I.D., filled with 10 mm ZnO for the analysis of acids and with ZnO mixed with Chromosorb W AW (80–100 mesh for the other analyses. The reactor was plugged with silanized glass wool.

RESULTS AND DISCUSSION

The microreactor is simple in construction and can easily be removed for refilling or replacement. It is independent of the temperature of the GC column, and

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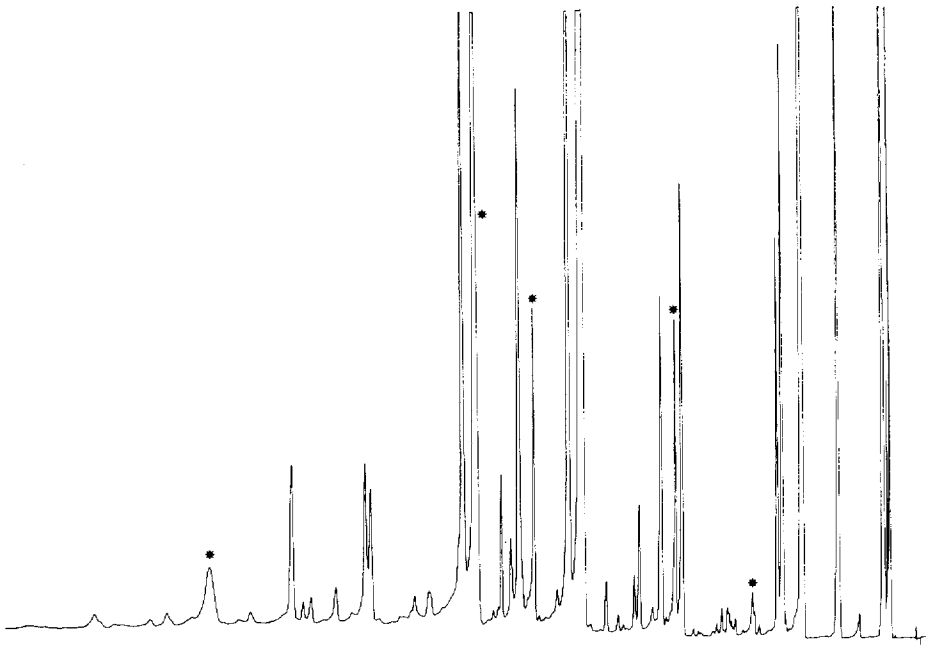

Fig. 1. Chromatogram without microreactor of aroma of wine extract (Chianti Classico, vintage 1977) *, Peaks subtracted by microreactor (see Fig. 2).

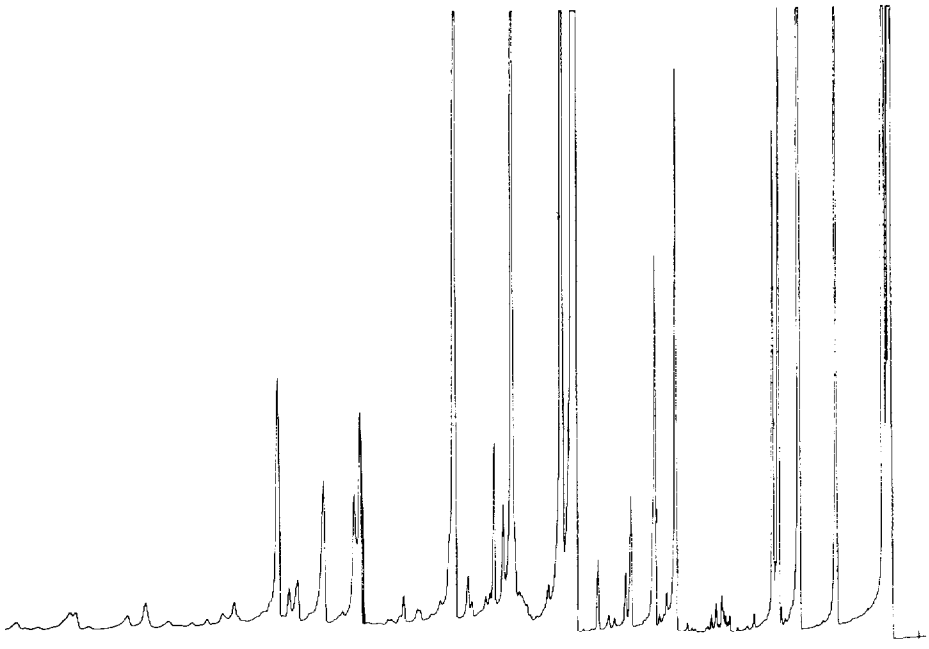

Fig. 2. Chromatogram with microreactor of aroma of wine extract (see Fig. 1).

has been successfully used for the selective removal of organic acids from a complex mixture. The carboxylic acids were retained quantitatively.

The compounds used for evaluating the efficiency of the microreactor were selected because of their structural differences and range of boiling points. The compounds subtracted were determined by comparing the chromatograms obtained with and without the microreactor inserted in the instrument. The retention time increased with insertion of the microreactor.

The reaction of a functional group (–COOH) with a reagent in the GC system to remove a compound by its conversion into a non-volatile derivative is one of the applications of chemical modification.

Fig. 1 (without subtractor) and Fig. 2 (with subtractor) are examples of the analysis of a complex mixture, obtained from natural products, in this case represented by aroma concentrates of volatile compounds, isolated from wine (Chianti Classico, vintage 1977).

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