

APPLICATIONS OF THE PYROCHROM™ FOR ON-LINE ELEMENTAL ANALYSIS OF GAS CHROMATOGRAPHIC EFFLUENTS*

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ABSTRACT

Applications are presented for the use of chromatographic stop-flow and a dual two-stage reactor unit in the Pyrochrom™ Elemental Analyzer for identification of gas chromatographic effluents. Illustrations of functional group and C, H, N, O analyses are given for complex organic mixtures. Sub-microliter samples are routinely analyzed within approximately 0.5% accuracy limits in a reliable and efficient manner to provide effluent on-line elemental analysis and subsequent empirical formula determination.

INTRODUCTION

Identification of trace levels of organic species which elute from gas chromatographs (g.c.) has been a difficult analytical problem for many years. Since the chromatogram gives no direct structural information, workers have turned to ancillary techniques for peak identification. It has been shown, in addition, that small molecule pyrolysis can be structurally informative, giving data similar to that from mass spectrographic analysis¹. Our concern for appropriate chemical information being obtainable in a realistic time for organic chemists and analysts, with or without computer availability, led to a combined engineering-design and development program by the Chemical Data Systems Corporation and the Armstrong Cork Company. This project resulted in a new, relatively simple, and inexpensive general tool which is rapid and accurate for the analysis of gas chromatographic effluents. On-line determination of the empirical formula of a g.c. peak has been accomplished in lieu of spectroscopic or trapping equipment.

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RESULTS AND DISCUSSION

We have previously presented the original design for the modular reactor system and data treatment¹⁻². An advanced modification of the PyrochromTM Elemental Analyzer, originally established for controlled thermolytic-dissociation patterns and functional-group analyses of g.c. effluents, now includes a dual two-stage reactor system.

Experimentally, Fig. 1 shows schematically the equipment necessary to obtain such empirical-formula data on samples directly injected into the PyrochromTM or as transferred species in a gas stream from a remote g.c. # 1 unit.

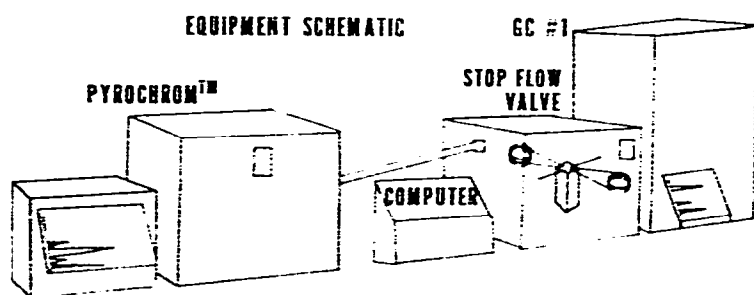


Fig. 1. Equipment schematic for trace organic analysis.

The flow scheme necessary to accomplish the detailed analysis has been shown previously². Whether or not the sample is a direct injection or a transferred peak, one has the option to bypass the reactor system and analyze further on the internal PyrochromTM chromatographic column or to send the sample through either of two reaction sequences. There are dual reactor lines, one of which is filled in two stages with catalysts to accomplish the oxidation-reduction (CHN) analysis, while the other reactor line is maintained for noncatalytic, functional-group analysis. For CHN and O analysis, the latter reactor line contains a Pt/carbon catalyst for oxygen determination by conversion to CO.

In order to perform these analyses, whether they be the catalytic C, H, N, O determination or functional-group study, a unique stop-flow arrangement briefly noted in our work² was set up in g.c. # 1. A sample could thus be injected into the analytical chromatographic column of g.c. # 1, separated in the usual fashion, a valve turned to stop-flow for each peak as it emerged, and subsequent analyses could then take place. The approximate 8-minute time delay for each of such determinations caused no noticeable peak shape or relative retention-time variations in the original chromatogram. This was illustrated by a four-component mixture of 1-microliter total volume being separated and each peak transferred through the noncatalytic functional-group reactor line and analyzed on the PyrochromTM internal column. Within 45 minutes, the identification of a hydrocarbon, ester, ketone, and alcohol had been accomplished. The species may also be directed through the catalytic CHN reactor line and identified according to its corresponding elemental analysis.

Illustration is given below for the approach taken for an unknown mixture of compounds using a 1-microliter total sample injection into g.c. # 1. A chromatogram is obtained for the complex mixture typically encountered for trace organics within the pollution-analysis field (Fig. 2). Two peaks, appearing in approximately 5 and 70

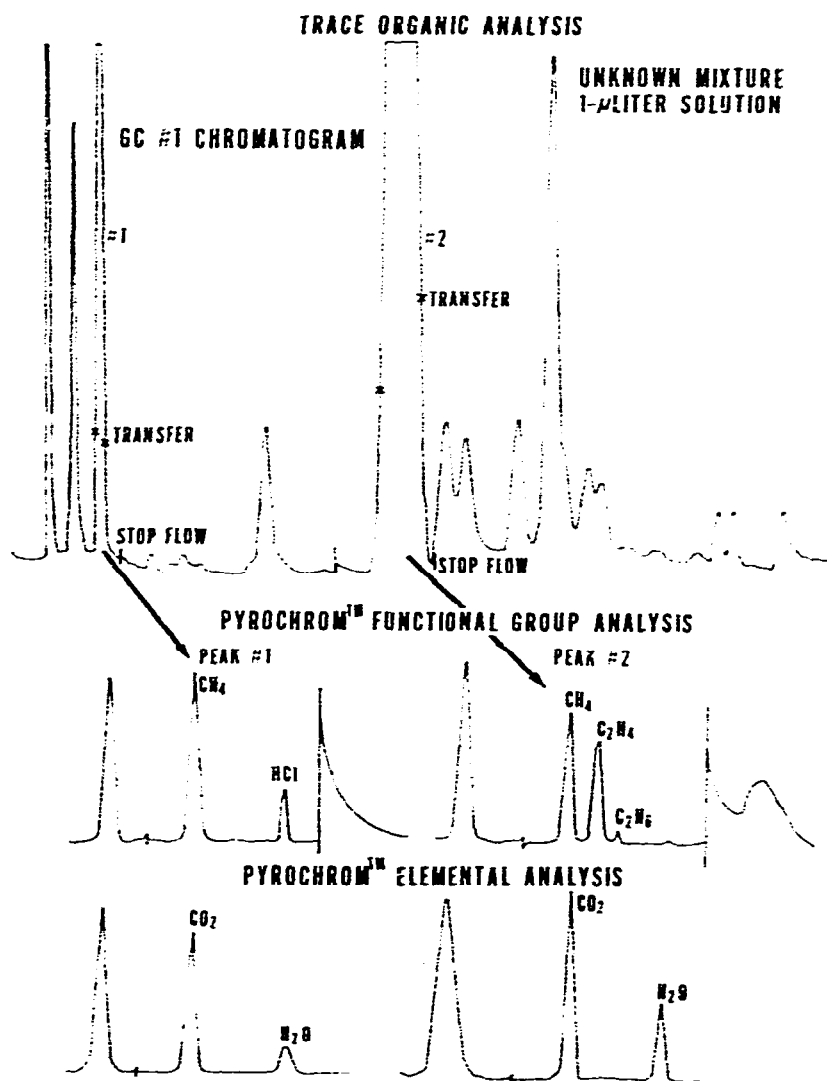


Fig. 2. Trace organic analysis for an unknown 1-microliter solution.

percent concentrations, were chosen for sequential analysis and their functional-group data from one reactor line were determined. Then, the corresponding elemental-analysis data were obtained from the other reaction line. With this information, either from deductive organic chemistry or computer-generated formulae which could conceivably have these combined data, the chemist is equipped to identify the species. Within an hour, separation, transfer, analysis, and interpretation can be completed on a 1-microliter sample.

An example is also shown of an application to polymer chemistry and degradation studies (Fig. 3). The polymer sample was pyrolyzed and a typical pyrogram consisting of more than a dozen peaks was obtained. Certain components in a pyro-

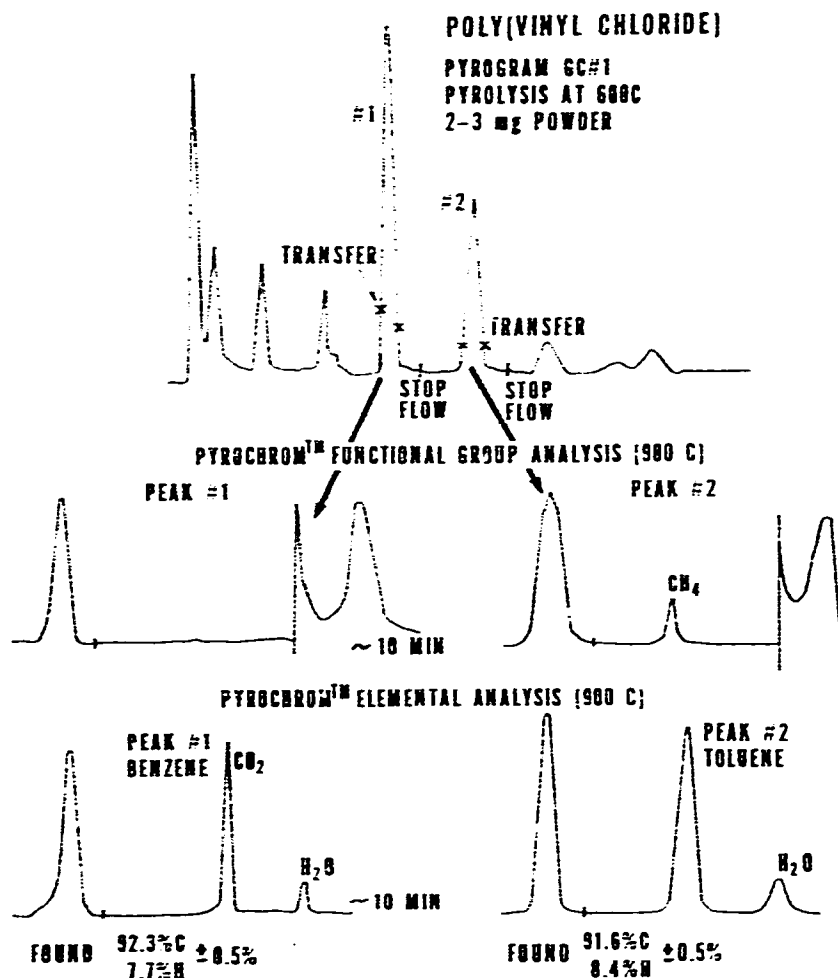


Fig. 3. Trace organic analysis for 2-3 milligrams solid polymer.

gram from poly(vinyl chloride) are of specific interest as they may relate to trace amounts of additives from the polymerization process which become involved in the degradation mechanism or to the basic microstructure of the polymer system. The functional-group analysis for these selected species was obtained, as well as their elemental data; the deduced structures were those of benzene and toluene. Again within an hour, significant analytical information had been generated on a polymer sample of 2 to 3 mg undergoing pyrolysis/degradation.

CONCLUSIONS

It is concluded that direct, chemically informative data can be obtained on minute samples emerging as effluents from a g.c. unit or directly injected into the PyrochromTM Elemental Analyzer. As for most cases in organic analysis, complementary methods are utilized to solve complex mixture and structure problems in an optimum fashion. We now have a commercially available tool that combined microchemical and reaction organic chemistry to the powerful capabilities of gas chromatography. In certain cases, even further confirmatory data beyond functional group, elemental analysis, and g.c. retention time may be needed to complete an identification. However, for an overwhelming number of situations found in industrial research or consulting laboratories, or for individual organic chemists studying polymer characterization, reaction mechanisms, kinetics, catalysis, or proof of structure, this direct and concerted analysis in a realistic time appears to be sufficient.

The further use to extend specialty elemental analysis to other heteroatoms by catalytic means and establish minimum detectable limits for the analyses will continue, as will applications to problem-solving for research, development, and processing situations at the Armstrong Cork Company.

REFERENCES

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