CHROM. 4376

An inexpensive and efficient pyrolysis unit for the analysis of picloram and other herbicides by thermal decomposition

Recently we found that picloram (4-amino-3,5,6-trichloropicolinic acid) could be quantitatively analyzed by electron-capture gas chromatography via thermal decarboxylation[1] rather than by esterification[2–4]. The decarboxylation technique has many advantages over the esterification method. For example, picloram in water, soil, or forage can be easily determined. This method should be applicable to other benzenoid herbicides and pesticides which have carboxyl of ester groups.

Commercial pre-column pyrolysis units are generally expensive and some expose the sample to a metallic heating element, thus making them incompatible with electron-capture detectors. There is, therefore, a need for an inexpensive and efficient pyrolysis unit which is specifically constructed for this purpose and which will not impair normal use of the gas chromatograph. We have constructed such a unit; its adaption to a Barber Coleman Model 5630 gas chromatograph fitted with an electron-capture detector is described below.

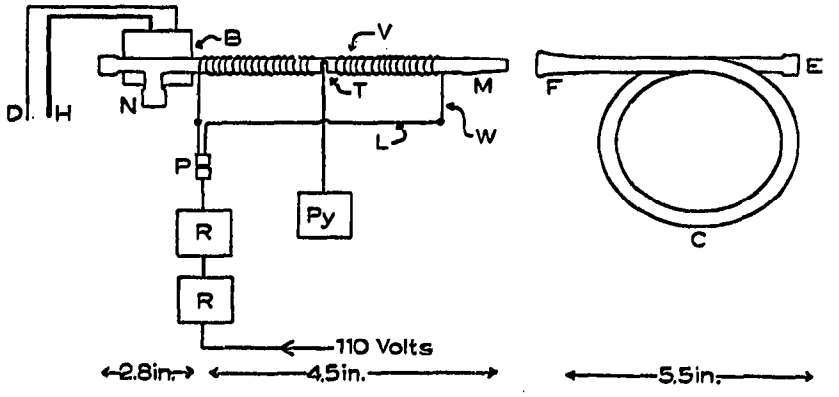

Fig. 1. Schematic of pyrolysis unit. D = thermocouple lead from chromatograph; H = cartridge-heater lead from chromatograph; N = nitrogen and injection inlet "tee"; B = injection heater block; P = male and female 110-volt plug; R = rheostat; V = vycor tube; T = thermocouple; Py = pyrometer; L = insulated copper lead; W = nichrome wire lead; M = male vycor ground-glass joint; F = female vycor ground-glass joint; C = 6-ft. spiral glass column; E = sample exit to electron-capture detector.

The following modifications were made to the chromatograph and column: the aluminum injection port heater was removed and the thermocouple leads were rerouted to the exterior through a hole in the extreme lower left-hand corner of the voltage control plate. A 6-ft. spiral glass column was cut 4.75 in. from the injector tip, and a female vycor ground-glass (10/30) joint connected to the column through a graded seal.

The pyrolysis unit (Fig. 1) was constructed by joining the nitrogen and injector inlet "tee" (N) to a vycor tube that was 4.5 in. long and 5 mm in inside diameter. As much soft glass as possible was eliminated between the "tee" and the vycor tube. A male ground vycor (10/30) joint (M) was connected to the other end of the vycor tube.

The aluminum block heater was installed on the inlet "tee" and covered with asbestos board (0.25 in. thick) which was held in place by copper wire. A thermocouple well was made in the center of the vycor tube and a Chromel–Alumel thermocouple inserted and held in place with asbestos putty. The tube was then uniformly wound with 26-gauge nichrome wire, each wind being separated by a wind of asbestos string. Three layers of asbestos string were then wrapped around the tube for insulation. The nichrome wire leads were connected to a 110-volt plug through 3-ft. lengths of insulated copper wire.

The pyrolysis unit was inserted approximately one-third of the way through the injection port and connected to the column, without grease via a male–female joint (M, F). The connection was secured with a No. 18 ball-and-socklet clamp. The portion of the pyrolysis tube exposed to the exterior was covered with fiberglass insulation. The rheostats connected in series were used to control pyrolysis temperatures. The pyrolysis unit was supported by a 3-finger clamp fastened to the exterior of the chromatograph.

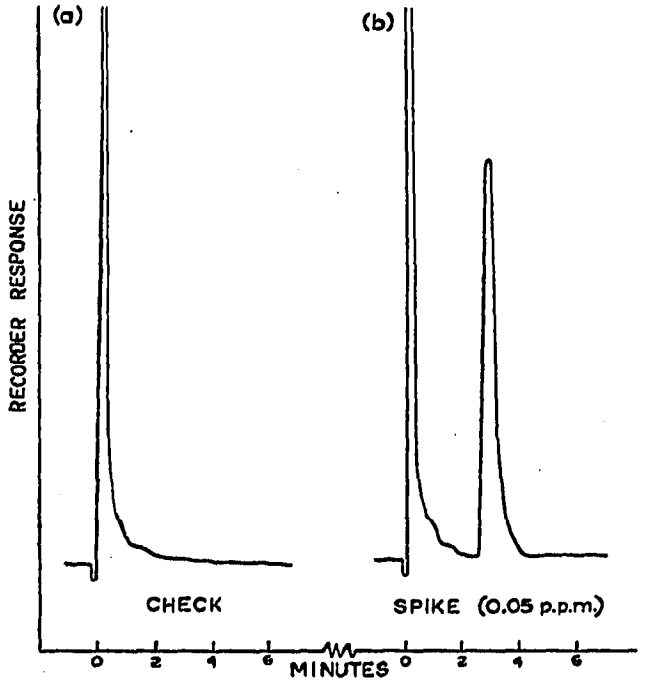

Fig. 2. Representative chromatograms of the decarboxylation of picloram obtained with the pyrolysis unit described herein. a = solvent; b = solvent plus picloram (0.5 μg per ml).

We have found that this unit, using vycor chips as an inert contact material, gave excellent results[1]. Due to the selectivity of this procedure, chromatograms are free from impurity peaks (Fig. 2) thus, making this technique ideal for trace analysis of herbicides in samples of high organic content. A detailed procedure employing thermal decarboxylation will be presented at a later date.

We wish to thank the Robert A. Welch Foundation for a predoctoral scholarship to S.D.A., and Dr. M. G. MERKLE for the use of his gas chromatograph.

Department of Chemistry,
Texas A&M University,
College Station, Texas 77843 (U.S.A.)

SCOT D. ABBOTT
R. C. HALL
C. S. GIAM*

1 R. C. HALL, C. S. GIAM AND M. G. MERKLE, unpublished results.
2 E. L. BJERKE, A. H. KULSCHINSKI AND J. C. RAMSEY, *J. Agr. Food Chem.*, 15 (1967) 469.
3 E. A. WOOLSON AND C. I. HARRIS, *Weeds*, 15 (1967) 168.
4 M. G. MERKLE, R. W. BOVEY AND R. C. HALL, *Weeds*, 14 (1966) 161.

Received September 15th, 1969

* To whom all correspondence should be sent.

CHROM. 4386

Thin-layer chromatographic separation of Δ-fac(N) and Δ-mer(N) isomers of tris(S-(+)-α-alaninato)cobalt (III)

α-Amino acids, which are bidentate ligands, coordinate around Co^{3+} in either $\Lambda(C_3)$ or $\Delta(C_3)$ absolute configuration (PIPER's notation[1]), while the unsymmetrical character of these ligands leads to geometrical isomerism. Many of the stereochemical questions are connected with both the rapid and the efficient separation of possible isomers. In the case of S-(+)-α-alanine, four isomers are known[2,3]: Λ,Δ-fac(N) and Λ,Δ-mer(N). From these, the Λ-fac(N) isomer is quite insoluble in water and the Λ-mer(N) one is only sparingly soluble. In the present note we describe the separation of geometrical isomers of Δ configuration with the axial disposition of CH_3 groups (k'k'k' arrangement of chelate rings, ob conformation with the C–C chelate axes oblique to the C_3 axis of rotation[4])(Fig. 1).

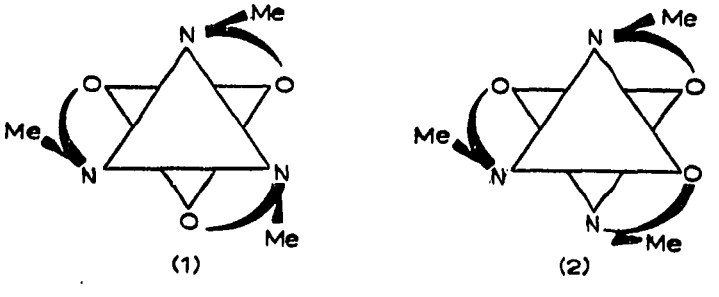

Fig. 1. Δ-Fac(N) (1) and Δ-mer(N) (2) isomers of Co(S-(+)-α-alaninate)$_3$. Projection around C_3 axis of rotation.