

atmosphere until the liquid became faintly yellow. As the addition of sulfur progressed, it became necessary to heat the reaction mixture sufficiently to melt the sulfur. As prepared, the tri-*n*-butylphosphine sulfide contained small amounts of unreacted sulfur and tri-*n*-butylphosphine. Tri-*n*-butylphosphine sulfide is now available commercially.

Procedure. The distribution ratio, *D*, was measured using gamma-emitting radioisotopes. The activity of each phase was determined by counting in a gamma-scintillation counter. Carrier solutions contained approximately $10^{-3}M$ of the metal. A 5% (v./v.) solution of tri-*n*-butylphosphine sulfide in CCl_4 was used. Equal volumes, 10 ml., of both phases were contacted for a period of 30 minutes. Phase separation was assisted by centrifugation at 2000 r.p.m. for 10 minutes.

Elements for which suitable radio-tracers were unavailable were checked using flame spectrometric methods. For these, 0.1*M* solutions of the reagent in cyclohexane were used.

RESULTS AND DISCUSSION

The results of the survey of 24 elements are listed in Table I. Similar

studies have been reported for three trialkylphosphine oxides by Ross and White (6, 7).

Tri-*n*-butylphosphine sulfide is much more selective than the trialkylphosphine oxides. Only two metal ions among those tested extracted well, silver(I) (*D* = 625) and mercury(II) (*D* = 282), both class *b* acceptors according to Ahrland, Chatt, and Davies (1). Elements which are partially extracted are border region acceptors and included bismuth (*D* = 0.56), copper(II) (*D* = 0.026 from 0.1*M* HCl), lead (*D* = 0.27), and zinc (*D* = 0.27). The pronounced selectivity of the reagent for silver and mercury is in accord with that reported for neutral phosphate esters containing a thiophosphoryl group, such as tri-*n*-butyl- or triisooctyl thiophosphate (3), but contrasts sharply with the behavior observed for trialkylphosphine oxides. The latter compounds react largely with class *a* acceptors. Triphenyl phosphine sulfide in $CHCl_3$ also extracted silver (*D* = 520) well from 6*M* HNO_3 .

It proved very difficult to strip mercury(II) from the organic phase with common reagents such as nitric acid, aqua regia, or sodium peroxide.

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CORRESPONDENCE

Determination of Hydrogen Cyanide and Cyanogen by Gas Chromatography

SIR: In the course of a study of the reactions of hydrogen cyanide, we have developed a chromatographic method for the determination of hydrogen cyanide and cyanogen. Woolmington (2) separated hydrogen cyanide, water, and nitrogen with a column of Celite or Chromosorb impregnated with 20% polyethylene glycol 1500. On the basis of his results and the solubilities of hydrogen cyanide and cyanogen, we examined columns of Chromosorb coated with several moderately polar, low molecular weight liquids for the separation of hydrogen cyanide, cyanogen, and carbon dioxide. Glycerol, diethylene glycol, and triethanolamine were not suitable, but triacetin (glyceryl triacetate, No. 256, Eastman Chemical Products, Inc.) or tributyrin (glyceryl tributyrate, No. 726, Eastman) effected the desired separation. Triacetin seemed to give better results. A triacetin column can be used for short periods at 90° C. and for several months

at 60° to 75° C. Triacetin separates chlorine and cyanogen chloride also, but the effect of continued exposure of the column and the instrument to these gases is not known.

Type 5A or 13X molecular sieve (Wilkins Instrument and Research,

Inc.) was used as received to separate oxygen, nitrogen, methane, and carbon monoxide. Each material also resolved nitric oxide in the absence of oxygen and methane.

Two columns, each prepared from 1/4-inch (5 mm. i.d.) copper tubing, were used in series. The first column

Table I. Retention Time and Volumetric Factors

| Component | Retention time, minutes | | | Volumetric factor, ^a <i>K'</i> , with molecular sieve | |
|-------------------|-------------------------|-----------------|------|--|-------------------|
| | Triacetin | Molecular sieve | | 5A | 13X |
| | | 5A | 13X | | |
| CO ₂ | 0.54 | ∞ ^b | ∞ | 1.38 | 1.25 |
| Cl ₂ | 0.80 | ∞ | ∞ | — | — |
| (CN) ₂ | 1.02 | ∞ | ∞ | 1.66 | 1.60 |
| O ₂ | 0.48 ^c | 1.70 | 1.46 | 1.00 | 1.00 |
| CNCl | 2.05 | ∞ | ∞ | — | — |
| N ₂ | 0.48 | 3.35 | 2.06 | 1.10 | 1.09 |
| HCN | 4.35 | ∞ | ∞ | 1.00 ^d | 1.00 ^d |
| NO | 0.48 | 5.33 | 2.87 | 1.03 | 1.06 |
| CH ₄ | 0.48 | 5.52 | 3.25 | 0.99 | 1.00 |
| CO | 0.48 | 15.3 | 4.00 | 1.00 | 1.18 |

^a Determined by method of Johns (1), based on peak area.

^b Irreversibly adsorbed.

^c Composite of permanent gases was eluted in 0.48 minute.

^d Determined with mixtures containing 35% HCN or less, *K'* = 1.00.

Table II. Analysis of Calibrating Gas Mixture

| Component | Composition, % | |
|-------------------|----------------|-------|
| | Known | Found |
| (CN) ₂ | 11.7 | 11.4 |
| O ₂ | 14.6 | 14.2 |
| N ₂ | 34.0 | 35.2 |
| HCN | 18.6 | 18.3 |
| CO | 21.0 | 20.8 |
| Total | 99.9 | 99.9 |

was 8 feet long and contained nonacid-washed 30- to 60-mesh Chromosorb P (Fisher Scientific Co.) impregnated with 25% triacetin; the second was 9 feet long and contained a molecular sieve. The triacetin column was operated at 75° C. and the molecular sieve column at room temperature. These two columns separated mixtures of cyanogen, hydrogen cyanide, oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide. Carbon dioxide was eluted from the first column immediately after the composite of permanent gases, so that in the presence

of more than about 25% of the permanent gases carbon dioxide was not separated completely. Water vapor was adsorbed by the triacetin column so that samples saturated with moisture at room temperature were analyzed with no tailing. HCN, (CN)₂, and CO₂ were irreversibly adsorbed on the molecular sieve column, but a single set of two columns was used for about 1000 analyses over a period of 6 months with no loss of effectiveness.

The chromatograph was equipped with a stainless steel dual column detector block with two matched-pair tungsten-filament elements that were operated at 75 ma. The 1-mv. recorder was operated at a chart speed of 1 inch per minute. The carrier gas, helium, was dried with silica gel and supplied at an inlet gage pressure of 18 p.s.i. and a rate of 108 ml. per minute at atmospheric pressure.

The chromatograph was calibrated by a method described by Johns (1) in which the peak areas from samples of pure gases are adjusted by factors, *K'* (used as divisors), so that equal volumes

of each gas give equal adjusted peak areas. *K'* for each gas was obtained by dividing the peak area for a known volume of the gas by the peak area for the same volume of another gas (O₂) chosen arbitrarily as a standard. The factors and retention times for several gases are listed in Table I. One anomaly was noted: with pure HCN, *K'* was high and erratic, but with mixtures containing less than 35 percent HCN, *K'* for this gas was 1.00 with either type of molecular sieve. Results of analysis of a calibrating gas mixture with triacetin and molecular sieve 5A columns are shown in Table II.

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Prevention of Peak Tailing in the Direct Gas Chromatographic Analysis of Barbiturates

SIR: The analysis of various barbiturates using the pyrolysis-gas chromatographic technique was first described by Janák (4-6). In his work, sodium salts were pyrolyzed and the products then were analyzed on a gas chromatograph. Nelson and Kirk, in a very recent work (7), also reported detailed studies on the pyrolysis of sodium salts and free acids. In the work of Cook *et al.* (3), the 1,3-dimethyl derivatives of various barbiturates were analyzed without pyrolysis on a gas chromatograph. Finally, the direct analysis of free barbiturates was described in three recent papers (2, 7, 8).

For the direct gas chromatographic analysis of barbiturates, liquid phases such as SE-30 silicone rubber gum, Apiezon L grease, FS-1265 fluorinated silicone oil, and polyesters were used on standard diatomaceous earth type (acid-base-washed Firebrick and Chromosorb W, Gas Chrom P) support material. Because the liquid phases were applied in low concentrations (usually below 5% w./w.), the barbiturate peaks tended to tail because of their partial adsorption on the solid support.

At the 1961 Lansing meeting, Averill (1) described the possibilities for the elimination of peak tailing when using certain cationic or anionic additives to the liquid phase. We found that by using hexamethyldisilazane (HMDS)-treated support material (9) and adding certain acidic additives (corresponding to the acidic character of the samples)

to the solid support, the active sites could be neutralized and, thus, symmetrical peaks could be obtained.

EXPERIMENTAL

A Perkin-Elmer Model 800 gas chromatograph equipped with a differential flame ionization detector was used for these studies. The columns were

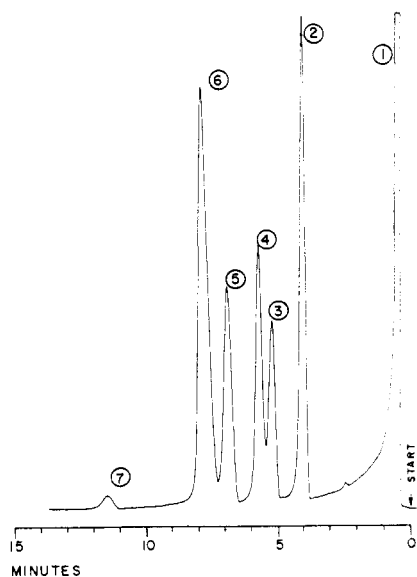


Figure 1. Chromatogram of (1) acetone, (2) barbital, (3) probarbital, (4) diallyl barbituric acid, (5) butethal, (6) amobarbital, and (7) hexobarbital

Carrier gas: helium, 27.8 ml. per minute.
Temp. of injection port, column, and detector: 280°, 180°, and 170° C., respectively

6 feet long, with 1/8-inch o.d. and 0.085-inch i.d.

The support materials were prepared in the following manner:

To 19.55 grams of 80 to 100 mesh HMDS-treated Chromosorb W, a solution of 0.15 grams of Empol 1018 dimer acid was added and then evaporated to dryness. The HMDS-treated Chromosorb W is a product of Johns-Manville Corp., New York 16, N. Y., and Empol 1018 is a product of Emery Industries, Inc., Cincinnati 2, Ohio. The latter consists of 80% dimer acid (a C₃₆ dibasic acid) and 17% trimer acid (a C₅₄ tribasic acid) with trace amounts of residual C₁₈ monobasic acids. The prepared support material was then coated with a solution of 0.3 gram SE-30 silicone rubber gum (a product of General Electric) in trichloroethylene, in the usual manner. This procedure gave a concentration of 0.75% dimer acid and 1.5% SE-30 on the support material.

To 19.25 grams of 80 to 100 mesh HMDS-treated Chromosorb W, a solution of 0.15 grams of Emery 3162-D trimer acid was added and then evaporated to dryness. The latter is approximately 90% trimer acid and 10% dimer acid. This prepared material was then coated with a solution of 0.6 gram of neopentyl glycol adipate (Analytical Engineering Laboratories, Inc., Hamden, Conn.) in trichloroethylene in the usual manner. This procedure gave a concentration of 0.75% trimer acid and 3% neopentyl glycol adipate on the support material.

The columns were packed with the aid of a vibrator, coiled, and operated at 180° and 200° C., respectively. The flow rates were 27.8 ml. per minute