Journal of Chromatography, 238 (1982) 445–456
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,667

GAS CHROMATOGRAPHIC METHODS FOR THE ANALYSIS OF TRACE QUANTITIES OF ISOPROPYL METHYLPHOSPHONOFLUORIDATE AND ASSOCIATED COMPOUNDS, *IN SITU* AND IN DECONTAMINATION EFFLUENT

SAMUEL SASS*, TIMOTHY L. FISHER, RALPH J. STEGER and GEORGE A. PARKER
Research Division, Chemical Systems Laboratory, Aberdeen Proving Ground, MD 21010 (U.S.A.)
(Received December 18th, 1981)

SUMMARY

Sample preparation procedures and quantitative analytical methodology were investigated for the trace determination (nanograms to picograms) of isopropyl methylphosphonofluoridate (GB) in decontamination media. Systems have been developed wherein residual GB and some related compounds can be extracted from chemically hostile media (compound half-life of seconds) and estimated by gas chromatography using an EGSS-X column and flame photometric detector. Intact GB is determined in the presence of much higher quantities of associated organophosphonates and other compounds.

INTRODUCTION

The primary objective of this work was to develop an accurate, highly sensitive, gas chromatographic (GC) method for determining trace levels of the highly toxic isopropyl methylphosphonofluoridate (GB). The method should be applicable to samples originating from land reclamation, pollution abatement, surveillance, decontaminated sites, and residues and effluent from clean-up processes.

The monitoring requirements established for prudent control of GB associated operations were set as follows: $3 \cdot 10^{-3}$ mg/m^3 in stack effluent; $3 \cdot 10^{-4}$ mg/m^3 maximum-permissible ground-level concentration; <1 ppm on a w/w basis for solid materials.

Included in the study was the additional requirement for developing suitable sample preparation procedures which would be totally compatible with the analytical method developed here. The requirements for sample preparation included considerations involving possible trace quantity synthesis of GB within a sample workup procedure, or via condensation reaction during GC analysis; also possible decomposition of agent GB which might be contained in original samples prior to workup; and finally the optimization of GB concentration in the analysis medium to insure that minimal levels of residual GB would be determinable.

The very first reported and recommended method for the gas chromatography of GB in the presence of its impurities[1] employed as a substrate DC-LSX-3-0295 on

0021-9673/82/0000–0000/$02.75

60–80 mesh Gas-Chrom P. This system, operating in the thermal conductivity detection mode, was found applicable for the quantitative determination in mixtures of GB, 2-propanol, methylphosphonodifluoride (difluoride), diisopropyl methylphosphonate (DIMP), and the GB pyroester, bis(isopropyl methylphosphonic) anhydride, among others. Furthermore, it was found at that time that isopropyl methylphosphonic acid (IMPA) could disproportionate on a GC column to form DIMP and possibly the methylphosphonic acid (MPA)[1]. Other column systems tested at that time included dioctyl and didecyl phthalate, silicone oil 200, silicone grease, and the Apiezons (J, L, and M), all on Johns-Manville firebrick. Only the Apiezon M approached the versatility of DC-LSX-3-0295 for analysis of GB in the presence of its impurities[1].

Previous related studies on some of the compounds described herein included GC–flame photometric detection[2] and GC–chemical and electron ionization mass spectrometry (MS)[3].

The work reported here, concerning the preparation of samples and the subsequent analytical methods employing gas chromatography, was the result of studies performed in this laboratory on hundreds of the various types of process samples. A large portion of these samples was from stack bubblers, brines, salts, and others related to a demilitarization program and had as their source spray dryer systems after chemical decontamination. The bulk composition of the brines and salts had been studied via infrared and Raman spectrometry[4] as well as by chemical analysis.

All of the GC column systems studied here were found applicable to the trace determination of GB. That found most useful for the determination of GB in media containing relatively large amounts of tributylamine (TBA) is a procedure employing a column packing of EGSS-X on Gas-Chrom Q.

PROCEDURES

Sample type and preparation

Three basic types of samples required analysis in support of a demilitarization program involving agent GB.

Water and stack bubbler samples originated from collection trains installed at various levels of the stack where the residual process gases were vented and dispersed into the atmosphere. The bubblers used for this sampling application contain an aqueous phase adjusted to pH 3.5 to pH 4.5 with sulfuric acid. Pretreatment, utilizing liquid–liquid extraction for concentrating these samples, was required to meet the low-level detection requirements of ambient air quality.

For gas chromatography, a 10-ml sample of the bubbler media was transferred to a clean 15-ml (conical-shaped) centrifuge tube and 2 g of sodium chloride were added and dissolved. Next a 0.1-ml portion of CP grade chloroform was added and shaken for no less than 1 min. The mixture was then centrifuged for 3 min and most of the upper layer (aqueous) was removed and discarded. The thin layer of water remaining inhibits the evaporation of the chloroform sample. A 1–20-μl sample of the chloroform solution was analyzed using the GC procedure described later. Water samples, as from suspected contamination, were handled similarly after adjustment to pH 4.5 with sulfuric acid.

The brine mixture was agitated to assure homogeneity. Brine, as a weighed 10–

15-g sample, was placed into a 100-ml beaker. A 50-ml buret was filled with 0.5 *N* sulfuric acid (precooled in an ice bath to <5°C). A 250-ml beaker containing 20 ml of cooled water was similarly placed in an ice bath positioned on a magnetic stirrer. A pH combination electrode was inserted in the 250-ml beaker which is used as the neutralizer vessel. Brine and cooled acid were slowly but simultaneously added to the water container in the neutralizer vessel. The pH was kept relatively constant at 7 ± 0.5 by varying the addition rates of the respective materials. The remainder of the brine was rinsed (with cold distilled water) into the vessel and adjusted to pH 6.5. The contents of the neutralizer vessel were quantitatively transferred to a graduated cylinder. Aliquots (10 ml) of this solution were transferred to individual centrifuge tubes. A 100-μl volume of chloroform was added to each tube for extraction purposes. The tubes were sealed with corks and shaken vigorously for several minutes. The tubes were then placed in a bench top centrifuge and the chloroform phase settled out after 3 min of operation.

Soil samples that had been decontaminated with sodium hydroxide or sodium carbonate could be similarly treated starting with the formation of a slurry by adding water containing TBA to a 5-g sample of the original soil. These samples were then handled in the same way as the brine mixtures.

After centrifugation was complete, about 9.5 ml of the water layer was removed and small microliter aliquots of the chloroform layer were injected into a gas chromatograph operated under prescribed conditions.

Salt samples were mixed thoroughly to insure homogeneity. Weighed 3.0 ± 0.5 grams of sample were placed into a 100-ml beaker. A 50-ml buret was filled with 0.5 N H_2SO_4 (precooled in an ice bath to <5°C). A 20-ml volume of cooled water and 30 to 50 mg of TBA were added to a 250-ml beaker, mixed and placed in an ice bath positioned on a magnetic stirrer. A pH combination electrode was positioned in the 250-ml beaker which was used as the neutralizer vessel. Salt and cooled acid were slowly but simultaneously added to the water contained in the neutralizer vessel. The pH was kept relatively constant at 7 ± 0.5 by varying the addition rates of the respective materials. The remainder of the salt was rinsed (with cold distilled water) into the vessel and adjusted to pH 6.5. The contents of the neutralizer vessel were quantitatively transferred to a graduated 100-ml cylinder for volume measurement and recorded. Aliquots (10 ml) of this solution were transferred to individual centrifuge tubes. A 100-μl volume of chloroform was added to each tube for extraction purposes. The tubes were sealed with corks and shaken vigorously for several minutes. The tubes were then placed in a bench top centrifuge and the chloroform phase settled out after 3 min of operation.

After centrifugation was complete, about 9.5 ml of the water layer was removed and small microliter aliquots of the chloroform layer were injected into a gas chromatograph.

The TBA added in the above procedure is apparently critical. In all of the salt samples tested, the omission of TBA addition resulted in very low or no recovery of GB "spikes". With the TBA addition, average recoveries of "spikes" of the order of 60% were obtained. This is comparable to the extraction efficiency expected.

An alternate procedure for treating the salts prior to analysis was also developed. This procedure incorporated trituration, with TBA added to the solvent prior to mixing.

The salt was mixed thoroughly to insure homogeneity. A 10.0 ± 0.5-g sample was weighed into a 40-ml screw top vial. A 500 μg TBA/ml chloroform stock solution was prepared for use in trituration (<25 ml required for each sample). The chloroform stock solution (10 ml) was added to the weighed salt sample. Using a glass "elephant's foot", the mixture was triturated for about 3 min. The mixture was then filtered through a Buchner funnel fitted with a Whatman No. 41 filter pad and the container and filter washed with several small portions (3 to 4 ml each) of the TBA–chloroform solution into a 25-ml graduated cylinder. The contents of the graduated cylinder were evaporated to near dryness and the remaining liquid measured in a 250-μl Hamilton gas-tight syringe (about 100 μl of solvent remained after evaporation in these experiments). Several 10–20-μl aliquots of the chloroform solution were injected into a GC system operated under the prescribed conditions.

The same procedure was applied to concrete and stone samples suspected of being contaminated with GB. The only additional preliminary step taken was to pulverize the sample to expose more surface area to the trituration solvent.

ANALYSIS BY GAS CHROMATOGRAPHY

Procedure for trace analysis of GB samples which contain TBA

The GC procedure developed for the trace analysis of GB samples containing TBA, originating from the demilitarization process where TBA is present, is given below. Any model gas chromatograph adaptable to an all-glass column and on-column injection system and fitted with a flame photometric detector system is suitable for this procedure. The conditions listed below are optimum when applied with a Perkin-Elmer Model 900 chromatograph and minor changes in the conditions listed may be necessary for optimum performance when operating other model instruments.

Column packing: 3% EGSS-X on 100–120 mesh Gas-Chrom Q.
Column dimensions: 6 ft. × 1/4 in. O.D. × 2 mm I.D. Pyrex glass.
Column temperature: Isothermal at 89°C for 2 min, then increasing 8°C/min to 200°C.
Inlet temperature: 180°C.
Detector temperature: 165°C.
Manifold temperature: 200°C.
Detector fuel gas flow-rate: hydrogen, 150 ml/min; oxygen, 15 ml/min; air, 15 ml/min.
Carrier gas (nitrogen) flow-rate: 20 ml/min.

Peak area measurements of the GB peaks are compared with the responses obtained on injecting standard solutions of GB in chloroform for quantitation. Calculations for parts-per-billion* or percent were made on the basis of original sample size and the aliquots used in the determination.

Alternate GC procedures for GB and related compounds

With the exception of the coatings mentioned below on 60–80 mesh Gas-Chrom Q all other parameters including flow-rates were identical to those employed with the EGSS-X column system described above and programmed from 60°C. The

* Throughout this article the American billion (10^9) is meant.

column with the 10% QF-1 coating was programmed at 8°C/min to 220°C. The column of 5% Carbowax 20M terminated with terephthalic acid (TPA) was programmed at 8°C/min to 220°, then isothermal for 4 min. The column of 30% DC-LSX-3-0295 was programmed at 8°C/min to 220°C. The column of 3% FFAP was programmed at 10°C/min to 240°C.

RESULTS AND DISCUSSION

Selection of column systems

The requirement for detection and estimation of extremely low quantities of GB with a high degree of specificity was exacerbated not only by the environmental media but especially by the nature of associated compounds and their decontamination products. Tests with a variety of column packings indicated that the GC methods employed for measuring trace quantities of GB might not be totally satisfactory for all types of samples requiring analysis. Thus, an improved GC method was sought with emphasis placed on moderate to highly polar column packings including Carbowax 20M terminated with TPA, QF-1, DC-LSX-3-0295, Tenax-GC, FFAP, and EGSS-X.

Carbowax 20M with TPA appeared initially to be a promising candidate for this application; however, interference at the elution time of GB was encountered when samples contained large quantitites of tributylamine (TBA, as high as 2 mg/ml), the stabilizer (neutralizer) used in some of the manufactured GB. An additional disadvantage of this carbowax column was its inability to elute the pyroester compound of GB [bis(isopropyl methylphosphonic)anhydride] as a sharp peak because of temperature limitations and retention characteristics.

A QF-1 column system[5–8] that had been adapted to a variety of agents in our laboratory was very successfully used for the analysis of VX and GB[2]. It was found very effective for monitoring low GB concentrations during the initial portion of this work. However, when high TBA concentrations were observed in subsequent samples, significant interference was encountered. The QF-1 column eluted the GB and its pyroester compound as distinct, sharp, resolved peaks in synthetic mixtures with low quantities (1–50 μg/ml) of DIMP. However, although the high DIMP concentrations (1–15 mg/ml) found in some samples did not affect the more rapidly eluting GB, they completely obscured the pyroester measurement area.

Attention was then focused on the slightly more polar fluorosilicone, DC-LSX-3-0295. A glass column, similar to that reported by Sass *et al.*[1] was selected since it had shown the capability for resolving a wide variety of GB-related compounds (including the pyroester) at higher concentrations. This column system, when incorporated into the GC–flame photometric detector (FPD) analyses of standard samples, gave good resolution of all of the volatile compounds, as in the macro system, but did not quite satisfy the need for sensitivity at the picogram level. The Carbowax and QF-1 systems provided detectability of quantities of GB at the 0.5 ng level. The DC-LSX-3-0295 system required more than 5 ng to achieve a comparable signal.

A solid adsorbent packed column containing Tenax-GC appeared very promising during the early phases of its evaluation. GB could be detected reproducibly at the extremely low levels found possible with both Carbowax 20M–TPA and QF-1.

TABLE I

RETENTION CHARACTERISTICS OF THE VARIOUS COLUMN SYSTEMS TESTED

Compound	*EGSS-X*		*QF-1*		*Carbowax 20M–TPA*		*DC-LSX-3-0295*		*FFAP*	
	Time (min)	*Temperature (°C)*	*Time (min)*	*Temperature (°C)*	*Time (min)*	*Temperature (°C)*	*Time (min)*	*Temperature (°C)*	*Time (min)*	*Temperature (°C)*
Chloroform (solvent)	0.4	75*	0.5	64	0.7	65	1.0	68	0.2	62
Diisopropyl-carbodiimide	1.0	75*	2.5	80	3.1	85	7.2	115	0.5	65
Tributylamine	1.4	75*	4.5	96	6.0	108	8.8	130	1.5	75
GB	4.8	104	5.0	100	5.1	101	9.9	140	2.5	85
Diisopropyl-methylphosphonate	7.6	120	9.2	134	9.6	136	13.1	165	5.5	115
Trimethyl-phosphine oxide	9.0	129	8.7	130	9.9	139	12.3	160	6.0	120
Diisopropyl urea	19.0	189	12.5	160	18.4	207	16.8	195	11.0	170
GB pyroester	21.8	206	18.4	207	20+**	220+**	19.0	200***	Did not elute	

* Program preceded by a 2-min isothermal period after sample injection; compounds detected by flame ionization, along with diisopropyl urea.

** Broad peak with gradual leading and tailing edges —not accurately quantifiable or reproducible for sensitive detection.

*** Temperature programmed to 200°C and held there for 4 min.

No column conditioning was required prior to obtaining satisfactory response. Synthetic samples containing TBA (64,000 parts) and GB (1 part) were sufficiently resolved to permit unambiguous GB measurement. Samples of IMPA (isopropyl methylphosphonic acid), the pyro acid bis(hydrogen methylphosphonic acid) anhydride and the pyroester of GB, as well as DIMP, trimethylphosphine oxide (TMPO) and MPA provided no interference to the analysis for compound GB. However, interferences were encountered when sample aliquots were injected from prepared solutions obtained from sulfur dioxide-injected salts and brines. This column packing material was summarily disregarded from further consideration as an analytical column in this application.

The EGSS-X column system performed extremely well in experiments conducted using the gas chromatograph with the FPD system. All of the components of interest were well resolved and detection thresholds were slightly better than those obtained with the Carbowax and QF-1 systems discussed earlier. Unlike the previously employed column systems, the EGSS-X column presented no difficulties in GB measurement or rapid baseline recovery when quantities of sample containing only 1 ng of GB and as much as 1.5 mg of TBA were injected. The polyester phases, of which EGSS-X is a member, are susceptible to hydrolysis at elevated temperatures. When this occurred some change in retention time and ultimate sample sensitivity was observed. The EGSS-X column was replaced with a fresh one when changes in retention time or sensitivity were noted. Rejuvenation of a fouled column using either Silyl-8 or Methelute were found to drastically alter the retention characteristics of this GC phase.

During the course of column screening, it was found that an FFAP system showed promise. Although GC–FPD data obtained using an FFAP column system was limited because of the earlier successes using EGSS-X, the preliminary data indicated this column material could be a satisfactory substitute if new problems arose because of process design changes. In fact, when the EGSS-X column was used in connection with GC–MS^3 applications via electron impact ionization, low-intensity ions were observed at *m/e* values of 99, 100, and 101. Since the *m/e* 99 ion measurement is critical in ascertaining the presence or absence of agent GB using this technique, the presence of these column background ions interfered with the determination. Thus, in GC–MS applications, the FFAP column was used with much success in later MS analysis of GB.

Of the various column materials tested, the five which resulted in the best resolution of components are listed in Table I. Included in this table are the retention times and elution temperatures for each compound on each system. The procedure employed with the EGSS-X column was reported in the experimental portion of this report. The other column systems as indicated were utilized under identical conditions except for the changes noted previously.

Sample preparation

Two of the most difficult sample mediums addressed in this study were brine and dried salt products derived through a caustic destruction process (*i.e.*, chemical disposal of the GB). The brine samples were aqueous slurries composed of approximately 30% solids. Once the brine samples were drum or spray dried, the resultant solids had to be certified that they were free of GB. The composition of these solids

included sodium hydroxide, sodium bicarbonate, sodium carbonate, the sodium salts of IMPA and MPA, sodium fluoride and sodium sulfate. Additionally contained in the solids could be residues of stabilizers such as TBA, diisopropylcarbodiimide, diisopropyl urea, and quantities of DIMP. The pH of the brines and reconstituted salts was greater than 12.8 and for the most part higher than pH 13. Therefore, either type sample provided a very hostile medium from which to manipulate any intact GB molecules into a suitable solvent.

Initial attempts at analysis of the GB salts involved trituration with a variety of solvents. All attempts to add known quantities of GB to the triturated mixtures resulted in little or no recovery of the added intact compound. GB hydrolyzes very readily at pH's of 10 and higher (half life $\approx$ 10 sec) and since small quantities of the compound could readily be reconstituted at pH 4 or lower with HF and IMPA present, the most favorable conditions for sample preparation should have been near neutrality. Even at temperatures controlled to 0–5°C and neutralization to pH 6.5–7.0 with 1 *N* sulfuric acid, "spikes" of GB produced unpredictable results and low recoveries. The cool acid neutralization technique was discarded in favor of a milder neutralization system as described in the procedure.

"Spiking" or adding known quantities of the GB to the material to be analyzed was undertaken to insure that GB was not being degraded by artifact of neutralization or the partitioning method. Its application was very important towards ascertaining the degree of recovery of actual compound that might be present in the substrate being analyzed. Near total recovery of such spikes was considered evidence that the sample preparation procedure would permit GB to be transferred intact to the analysis medium. The partial success observed in recovering GB spikes from brine, as opposed to the poor or no recovery from spiked salts, was suggestive that the spray dryer heat was removing from the salt some component(s) that was present in the brine. Two candidates considered were DIMP and TBA. The latter (TBA) was found in our studies to have the most influence in supporting the GB spike. The spiking of the brine samples was performed early in the preparation procedure. It was found that neutralized brine could support some of the GB spike. GB was added to the 20 ml of cooled water prior to the start of neutralization. The results for some spiked brines are shown in Table II.

The results of two spiking experiments on the salts are given in Table III. The samples (numbered 1–4) were run through the sample preparation procedure without

TABLE II

REPRESENTATIVE RESULTS OF SOME "SPIKING" EXPERIMENTS CONDUCTED WITH BRINES

Brine sample	*GB present (μg)*	*GB added (μg)*	*GB found (μg)*	*Recovered (%)*
A	None detected	9.66	4.50	27.0
B	None detected	9.66	4.56	47.2
C	None detected	9.66	5.76	59.6
D	None detected	9.66	5.76	59.6
E	None detected	10.30	6.28	60.9
F	None detected	10.30	6.19	60.1

TABLE III

RESULTS OF "SPIKING" APPROXIMATELY 3-g SAMPLES OF SPRAY DRY SALTS WITH GB

Sample	*Quantity of TBA added (mg)*	*Quantity of GB added (μg)*	*Quantity of GB found (μg)*	*GB recovered (%)*
Blank	0	0	None detected	—
1	0	19.3	4.1	21.0
2	0	19.3	4.1	21.0
3	0	19.3	4.0	20.4
4	0	19.3	4.3	22.3
Blank	35	0	None detected	—
5	35	482.9	394.9	61.3
6	35	482.9	397.2	61.7
7	35	482.9	384.0	59.6
8	35	120.2	69.8	58.1
9	35	120.2	74.8	62.2
10	35	120.2	72.7	60.5

adding the TBA found to be required in the salt analysis procedure. The other salt samples were "spiked" by adding GB to the cooled water mixture containing TBA prior to the start of neutralization.

In early trituration experiments, attempts to spike the salt directly were unsuccesful. A recovery of 1.6% was obtained in one experiment where a mixture of TBA (50 mg) and GB (500 μg) contained in chloroform was dispersed on a 3.5-g sample of a drum-dried salt.

A vigorous reaction took place during this spiking procedure as the amine odor was quite obvious and the salt (originally just off-white) turned very dark (almost black). The amount of DIMP formed was so great that it overloaded the flame-photometric detector.

Other experiments were then conducted where only 10 ml of TBA-containing chloroform (*ca.* 500 μg/ml) were added to each weighed salt sample. The TBA solu-

TABLE IV

RESULTS OF SOME "SPIKING" EXPERIMENTS CONDUCTED USING THE TRITURATION PROCEDURE WITH TBA ADDED

Approximately 10-g salt sample in each case.

Sample No.	*GB added (μg)*	*GB found*		*Recovery (%)*
		(μg)	*(ng)*	
1	536.6	430.0		79.9
2	0		<20	—
3	536.6	431.2		80.4
4	0		<20	
5	536.6	408.9		76.2
6	536.6	414.8		77.3
7	536.6	430.4		80.3

tion was allowed to wet the salts and then was shaken thoroughly for a few minutes. Exactly 1 ml of a 536.6 μg/ml solution of GB in chloroform was added to four of these samples and the mixture was shaken thoroughly for an additional 2 min. After allowing the solids to settle, an aliquot of the clear chloroform solution was removed for analyses via GC. The results of these experiments are shown in Table IV.

The results shown in Table IV demonstrate that, if intact GB were occluded within the dried salt structure itself (perhaps, within the lattice network of diisopropyl urea crystals), the TBA-containing chloroform solution could provide a means of extraction of the intact GB for subsequent quantitation.

All attempts to add GB to salts in the absence of significant quantities of TBA resulted in complete loss (*i.e.*, destruction) of the GB.

The same trituration procedure employing 500 μg TBA/ml chloroform was used to analyze a representative portion of the spray-dried salts obtained from a variety of sources which incorporated different drying parameters (*e.g.*, drum dryer, operating temperature changes, fuel changes, etc). The most notable conclusion that can be drawn from the found data was that no GB was found in any of the salt samples examined and that the DIMP values obtained were in a relatively constant range of 12 to 26 μg/g of salt irrespective of the operational parameters employed in the drying procedure.

The same trituration procedure has been used with success in analyzing soil, concrete, and exudate samples associated with GB disposal. The ability to maintain and recover a GB "spike" in these additional applications has been used as a gauge in determining the versatility of the developed method.

The results obtained, using the acid-demand brine procedure when applied to several authentic brine samples, are given in Table V.

In addition, water samples originating from a high-pressure concrete removal system were run to establish the presence of absence of agent to insure safe disposal. In this instance, salt (sodium chloride) was purposefully introduced into the water to aid in extraction of GB, and TBA was added in amounts of 5 mg/ml of water in the sample aliquot. This procedure provided for the effective transfer and concentration of known quantities of GB added to blank samples while insuring the agent's stability.

Bubbler solutions were the least difficult to handle and required only a minimum of sample pretreatment prior to analysis. The simulated bubbler solutions

TABLE V

RESULTS OF BRINE ANALYSES

Brine sample	*GB (ng/g)*	*DIMP (ng/g)*	*Apparent pyroester (ng/g)*	*TBA (mg/ml)*	*DICDI* (μg/g)*
1	15	9	5	1.1	–
2	5	10	1	1.5	–
3	<1	20	<1	1.3	<0.2
4	<1	19	<1	<0.1	2.2
5	≈1	31	<1	6.6	<0.2
6	≈2	18	<1	5.4	<0.2

* Diisopropylcarbodiimide.

TABLE VI

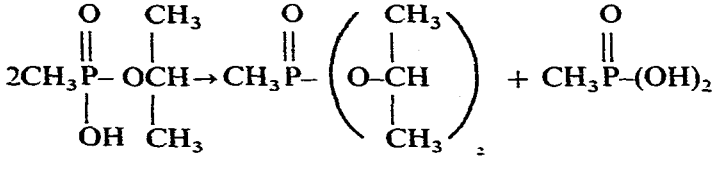
ANALYSES OF KNOWN SOLUTIONS OF GB IN pH 4.5 SULFURIC ACID

Sample	*Quantity of GB (ng)*		*Recovered*
	*Actual**	*Found*	*(%)*
1	96.3	99.3	103.1
2	96.3	98.0	101.8
3	325.0	309.0	95.1
4	192.6	197.0	102.3
5	96.3	96.2	99.9
6	48.2	48.4	100.4
7	96.3	98.9	102.7
8	30.0	27.6	92.0
9	400.0	375.0	93.8
10	96.3	98.1	101.9
11	192.6	190.8	99.1
12	15.0	14.4	96.0
13	48.2	47.0	97.5
14	325.0	304.0	93.0
15	30.0	31.0	103.3
16	400.0	382.0	95.5
17	96.3	100.0	103.8
18	30.0	26.6	88.7

* Corrected to the nanograms expected based on 60% solvent partitioning efficiency.

were dilutions of known amounts of GB in pH 4.5 sulfuric acid solutions. These samples were extracted in the identical manner as the unknown bubbler solutions. The results obtained on a series of the known solutions are listed in Table VI.

Some very interesting aritifacts had been observed in some of our early work[1] using the thermal conductivity detector. It had been found that in-column preparative reactions via disproportionation and condensation did occur and could result in highly misleading information. This becomes especially true and critical when GC is being used for the detection and estimation of nanogram and picogram quantities of substances. IMPA is a hydrolysis product of GB. If not removed during the analytical sample preparation procedure two molecules of IMPA can react to give the disproportionation products DIMP and MPA.



MPA does not elute from the column.

Similarly, it was found that IMPA and HF, if added to the extract, could react in-column to form readily detectable quantities of GB and DIMP. This artifact which could be totally defeating was precluded by following the developed, sample preparation procedure.

Each of the column systems reported here has proved to be highly useful depending on the application areas. The DC-LSX-3-0295 column, for example, was superior to the others in eluting the pyroester of GB. The FFAP column system proved most beneficial in mass spectrometry studies for GB and its associated components with the exception of the pyroester. The Carbowax 20M column was extremely useful when determinations of stabilizer type and quantity were desired. The QF-1 column system showed extremely long-term usefulness and performed satisfactorily in all cases except when TBA was present in gross excess producing a "quenching" effect at the retention time of GB. The Carbowax 20M column was similarly affected by high TBA concentration. The EGSS-X column system reported in the procedure section of this report represented the best all around compromise method for samples from a wide variety of sources. The minimum detectable quantity of GB determined with this system in a variety of different instruments was about 0.3 ng. The accuracy of the method at the 15-ng level was found to be ± 2.2 ng; while the calculated standard deviation at the 100 ng level was ± 1.3.

We have described some misleading artifacts that can occur due to undesired pre-column or in-column preparative reactions that reconstitute molecular species by condensation of their unseparated hydrolysis products. Also observed are new products that are synthesized by in- or on-column disproportionation of residues that have longer retention times in the column. Similar occurrences had been observed by our laboratory in the GC of some arylidinemalononitrile irritants[8] and some esters and amides.

ACKNOWLEDGEMENT

The authors are grateful to Mrs. Margaret Williamson for typing and reproducing this report.

REFERENCES

1 S. Sass, S. Pinsky and M. R. Barnes, *Chem. Syst. Lab CRDL Tech Memo 62-2*, Chemical Systems Laboratory, Aberdeen Proving Ground, MD, 1963.
2 S. Sass and G. A. Parker, *J. Chromatogr.*, 189 (1980) 331.
3 S. Sass and T. L. Fisher, *Org. Mass Spectrom.*, 14 (1979) 257.
4 R. J. Piffath and S. Sass, *Def. Tech Info Cent. (DTIC), AD A026736; EC-TR 76060*, Chemical Systems Laboratory, Aberdeen Providing Ground, MD, 1976.
5 T. L. Fisher, M. Jaskot and S. Sass, *DTIC, AD 858138; EATR-4321*, Chemical Systems Laboratory, Aberdeen Proving Ground, MD, 1969.
6 S. Sass and R. J. Steger, *J. Chromatogr.*, 238 (1982) in press.
7 S. Sass, T. Fisher and D. Thompson, *DTIC, AD 869379; EATR 4389*, Chemical Systems Laboratory, Aberdeen Proving Ground, MD, 1970.
8 S. Sass, T. L. Fisher, M. J. Jaskot and J. Herban, *Anal. Chem.*, 43 (1971) 462–464.