# **Determination of Gamma Isomer of Benzene Hexachloride**

Mass Isotope Dilution Method

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A mass isotope dilution method for the determination of the gamma isomer of 1,2,3,4,5,6-hexachlorocyclohexane is described. Gamma-hexadeuterobenzene hexachloride is used as the tracer molecule and the extent of isotopic dilution in the isolated gamma isomer mixture is determined by means of infrared spectrophotometry. The extension of this method to the determination of alpha, beta, and delta isomers, although of less practical importance because of their entomological inactivity, is also discussed. The infrared absorption spectra of the alpha, beta, and gamma isomers of hexadeuterobenzene hexachloride over the range of from 2.5 to 15 mu are presented.

 $\mathbf{E}$  VER since the discovery in 1943 by F. J. D. Thomas (12) of the insecticidal activity of the gamma isomer of benzene hexachloride, there has been interest in the development of reliable methods of assay for its determination, particularly in mixtures containing considerable amounts of the other four known isomers as well as other chlorination products of benzene.

Several methods of assay have come to the authors' attention. The first is based upon direct infrared spectrophotometry (4, 8). The second is a biological method involving the paralysis of 3day-old mosquito larvae of Ades aegypti (5). The third is based upon a solubility method (11), and the last upon lowering of melting point (2). The reliability of all these methods is obviously dependent to a greater or lesser degree upon the nature and amount of the nonbenzene hexachloride material present in any given sample being assayed. Thus some commercial crudes give erroneous results when assayed by direct infrared spectrophotometry. Moreover, it has been observed that such "background" material exerts a very definite effect upon the solubility behavior of the gamma isomer (11).

In view of this situation the authors decided to appeal to an approach that is not subject to these defects and is, therefore, absolute in the sense that the reliability (accuracy) of the result is determined only by the precision of the technique used. Such an approach is offered by the isotope dilution method. The simplest isotopic tracer to obtain and to introduce into a molecule like benzene hexachloride is, of course, the stable isotope deuterium. Consequently the present assay method is based upon the addition of a known amount of  $\gamma$ -hexadeuterobenzene hexachloride to a known amount of the sample to be assayed (if the assay of any of the other isomers is required, the appropriate alpha, beta, or delta hexadeutero isomer may be added). The whole mixture is then dissolved to render it homogeneous and a specimen of the mixed (isotopically) gamma isomers is isolated. The ratio of  $C_6H_8Cl_6$  to  $C_6D_6Cl_6$  in this isolated specimen is then determined by direct infrared spectrophotometry.

# PREPARATION OF HEXADEUTEROBENZENE HEXACHLORIDE TRACERS

There are two generally useful methods whereby deuterium may be exchanged for the protium in benzene. The first involves the use of deuterosulfuric acid (7); the second, catalytic exchange using deuterium oxide and a nickel catalyst at 200° to  $300^{\circ}$  C. (3). The second method was used.

To a mixture of 220 grams of purified benzene and 200 grams of (99.5%) deuterium oxide were added 1 to 2 grams of Raney's nickel catalyst (wet with benzene). The whole mixture was placed in a stainless steel hydrogenation bomb and after closing was heated at 250° C. with shaking until equilibrium had been

attained. The rate of reaction was followed by withdrawing small specimens of the benzene phase from time to time and examining their infrared absorption spectrum with particular attention to the magnitude of the C—H and C—D linear stretching frequencies at 3.26 and 4.36 mu, respectively. By this means it was found that about 60 hours were required to attain equilibrium. After cooling and separation of the phases, the partially deuterized benzene phase was returned to the bomb and treated with a fresh 200-gram portion of deuterium oxide and a fresh 1- to 2-gram portion of Raney's nickel catalyst and the 60 hour-heating period was repeated.

After five such treatments 195 grams of deuterized product were obtained. In order to determine the degree of deuterization of this material a small portion was purified.

Three grams of trans-4,4'-dihydroxy- $\alpha,\beta$ -diethylstilbene (diethylstilbestrol) were dissolved in about 40 ml. of the deuterized benzene and after standing for 17 hours at 23° C. the crystals of the benzene solvate of "diethylstilbestrol" were filtered off. The deuterobenzene was then recovered from this solvate by passing a slow stream of dried air through the heated (56° C.) crystals and collecting the deuterobenzene in an ice-cold trap. In this manner 1.2 grams of deuterobenzene free of cyclohexane, thiophene, etc., were obtained.

The infrared absorption spectrum of this purified product in the liquid state as determined on a carefully calibrated (10) Model 12A Perkin-Elmer infrared spectrometer was found to agree closely with that reported by Herzfeld, Ingold, and Poole (6) except for the presence of two moderately strong bands at 3.47 mu (3060  $\tilde{\nu}$ ) and 14.05 mu (711  $\tilde{\nu}$ ), neither of which was reported by the British workers. Because, however, the deuterobenzene used here is only 93 atom % deuterium while the British workers reported their deuterized benzene to be 99 atom %, it is possible that the 3.47- and 14.05-mu bands might arise from the 25 to 30 mole % of C<sub>6</sub>D<sub>5</sub>H present in the preparation. The authors were, however, unable to check this inference, since they have been unable to find infrared data for C<sub>6</sub>D<sub>5</sub>H. In determining the extent of deuterization of their product, they measured its density by means of a micropycnometer and computed the deuterium concentration from the density value for pure hexadeuterobenzene of  $d_{25}^{*5} = 0.94611$  given by Weldon and Wilson (16). For ordinary benzene they observed a density value of  $d_{25}^{*5} =$ 0.87580 and for their deuterobenzene  $d_{25}^{*5} = 0.94108$ . Combining these data with those of Weldon and Wilson they found that their benzene contained 93 atom % of deuterium, which they considered sufficiently good for their purposes. The chlorination of the deuterobenzene was carried out as fol-

The chlorination of the deuterobenzene was carried out as follows: One hundred and thirty nine grams of hexadeuterobenzene were treated with 150 grams of chlorine under a nitrogen atmosphere and irradiated by means of a G.E. sun lamp in a manner usual for photochlorinations. From this reaction 184 grams of crude benzene chlorination products were obtained and by fractional crystallizations in the usual manner (12) 12 grams of the pure gamma isomer of hexadeuterobenzene hexachloride (melting point 112.5 ° C.) were obtained.

A careful study of the melting point behavior of the gamma isomer to which small amounts of the other isomers had been

Table	I.	Infrared	Absorption	Bands
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	Wave Le	ngth, Microns	
$\alpha$ -C6D6Cls	β-C6D6Cle	$\gamma$ -C6D6Cl6	γ-C6H6Cl6
$\begin{array}{c} 13.80 \ \mathrm{S}^{\mathrm{s}} \\ 13.67 \ \mathrm{S}^{\mathrm{s}} \\ 12.91 \ \mathrm{M} \\ 12.70 \ \mathrm{W} \\ 12.38 \ \mathrm{M} \\ 12.20 \ \mathrm{W} \\ 11.95 \ \mathrm{M} \\ 11.84 \ \mathrm{M} \\ 10.91 \ \mathrm{S} \\ 10.43 \ \mathrm{W} \\ 10.38 \ \mathrm{S} \\ 9.89 \ \mathrm{S} \\ 9.24 \ \mathrm{W} \\ 8.84 \ \mathrm{S} \\ 8.91 \ \mathrm{W} \\ 8.847 \ \mathrm{S} \\ 8.47 \ \mathrm{S} \\ 8.47 \ \mathrm{S} \\ 8.47 \ \mathrm{M} \\ 3.41 \ $	14.28 S (broad) 13.00 W 12.56 W 12.30 W 11.67 S 10.10 M 9.00 W 9.72 S 9.37 M 9.10 S 9.05 S 8.72 M 7.96 M 4.46 M 3.41 M	) $13.77 \text{ S}$ (broad) 12.83  W 12.69  M 12.54  W 12.26  M 12.20  M 1.27  S 10.93  M 10.60  M 10.67  M 9.62  W 9.55  S 9.18  W 8.88  S 8.47  S 7.88  W 4.46  M 3.41  M	$\begin{array}{c} 14.90 \ \mathrm{S} \\ 14.50 \ \mathrm{S} \\ 14.21 \ \mathrm{S} \\ 12.80 \ \mathrm{S} \\ 11.77 \ \mathrm{S} \\ 10.97 \ \mathrm{M} \\ 10.50 \ \mathrm{M} \\ 10.28 \ \mathrm{W} \\ 9.94 \ \mathrm{W} \\ 9.75 \ \mathrm{M} \\ 9.75 \ \mathrm{M} \\ 9.06 \ \mathrm{S} \\ 8.41 \ \mathrm{M} \\ 8.20 \ \mathrm{W} \\ 7.96 \ \mathrm{M} \\ 7.96 \ \mathrm{M} \\ 7.96 \ \mathrm{M} \\ 7.40 \ \mathrm{S} \\ 3.41 \ \mathrm{M} \end{array}$
ties.	W multate strong,	mouerate, and weak at	sorption intensi

added has shown that the melting point is a very sensitive and reliable index of purity. The authors have observed that amounts of the alpha isomer added to the gamma isomer which are too small to be easily observed by infrared measurements are readily detected by the melting point behavior.

Specimens of some of the other isomers of hexadeuterobenzene hexachloride are, of course, also isolatable in pure form during the procedure for isolating the gamma isomer and these may be used in assaying for their respective isomers where required.

In Figures 1 to 4 and Table I are presented the infrared absorption spectra of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -hexadeuterobenzene hexachloride and of  $\gamma$ -hexaprotiobenzene hexachloride run as solid mulls in petrolatum. The infrared absorption spectra of the other known protio isomers are not presented because spectral measurements for them agree in every detail with those presented by other workers (4, 9).

Table II is the slit schedule used in obtaining the above spectra.

### SPECTROPHOTOMETRIC DETERMINATION OF ISOTOPIC DILUTION

A superficial inspection of the spectra of the two gamma isomers reveals that there are two intense absorption bands in each which are clearly suitable for use for the spectrophotometric determination of these substances. These are, for the solids, 14.51 and 11.74 mu for the protio isomer and 13.79 and 11.28 mu for the deutero isomer. In dimethyl formamide as solvent the corresponding absorption bands are shifted slightly and occur at 14.55 and 11.83 mu for the protio isomer and 13.75 and 11.21 mu for the deutero isomer.

It is, of course, possible to carry out the desired spectrophotometric analysis for the relative amounts of  $C_6H_6Cl_6$  and  $C_6D_6Cl_6$ using either solids or solutions, but as, in general, the authors have found solutions somewhat easier to manipulate, they have adopted them for regular use. Naturally, an involatile solvent is desirable for quantitative manipulation, and in looking about for a suitable one the authors found that dimethyl formamide has several properties which render it useful as a solvent for quantitative infrared spectrophotometry. Apart from its easy preparation and purification it has a high boiling, 153° C., and excellent general solvent characteristics (many sodium salts freely dissolve in it), and its infrared spectrum contains only one band (at 11.55





a. Bands due to petrolatum vehicle used in making absorption layers

Table III.	Infrared	Absorption	of	$\gamma$ -He	exaprot	tiobenze	n
Hexachl	oride	exadeuterob	enz	ene	Hexac	hloride	
	-	Mixtures					

	Optical	Density
$\begin{array}{c} \% \ \mathrm{CeDeCle}, \\ f\gamma D \end{array}$	d (slit 0.900) 13,75 mu	d (slit 0.500 11.83 mu
100	0.761	0.140
75	0.596	0.297
50	0.431	0.455
35	0.334	0.559
25	0.267	0.613
_0	0.100	0.767

mu) between 10 and 15 mu. Where the direct infrared analysis of the benzene hexachloride isomers is required, dimethyl formamide has an added advantage over solvents formerly used in that the beta isomer, being freely soluble, may also be determined along with the other isomers.

The most suitable conditions for making the desired optical measurements are a constant concentration of 200 mg. of sample per ml. (948 mg.) of purified (redistilled, boiling point 153 ° C.) dimethyl formamide placed in a sealed absorption cell of 0.10-mm. path length. Through the use of these conditions and by making up a series of known mixtures of the protio and deutero  $\gamma$ -benzene hexachlorides, the optical densities of such mixtures could be determined at the 13.75- and 11.83-mu bands, using the empty cell as the reference state. In this manner the calibration data presented in Table III were obtained.

Beer's law is followed closely, as would be expected of such a system as that under study here. Similar calibration curves could be established for the other isomers if desired. In analyzing mixtures of the  $\alpha$ -protio- $\alpha$ -deutero isomers the infrared absorption bands at 13.15 and 13.70 mu, respectively, could be used, while for the  $\beta$ -protio- $\beta$ -deutero isomer mixtures the 13.5and 14.35-mu absorption bands would serve. The authors have found that the absolute values of the calibration remain satisfactorily constant, provided the optical density of the solvent is maintained constant. This is best achieved by preparing a large batch of dried and purified dimethyl formamide and, having established the calibration curve through its use, setting it aside exclusively for these isotope dilution assays. Water in the dimethyl formamide is the worst offender and should be carefully guarded against. If the solvent-filled cell rather than the empty cell had been used as reference state I, much of the effect due to change in the solvent characteristics could have been avoided, but because their procedure proved entirely satisfactory and is simpler of manipulation the authors preferred to use it.

#### ISOLATION OF PURE GAMMA ISOMER FROM TYPICAL CHLORINATION CRUDES

In carrying out an analysis by means of the isotope dilution method it is of first importance to be able to isolate qualitatively a typical specimen of the pure molecular species for which assay is required. After considerable experimentation the following process was developed for isolating a specimen of the pure gamma isomer (isotopically mixed of course) of benzene hexachloride.

About 15 grams of the crude sample are weighed out accurately and dissolved in a 50-ml. volumetric flask containing acetone. So large a sample is taken to ensure average uniformity, as benzene hexachloride crudes are sometimes inhomogeneous physically. Exactly 5.0 ml. ( $W_{2}$ ) of the acetone solution are put into a suitable evaporation vessel and  $\gamma$ -hexadeuterobenzene hexachloride is added to the extent of about 15% of the weight of the dissolved crude (1.5 grams  $\times$  0.15 = 0.225 gram). This is weighed out exactly ( $W_{\gamma D}$ ) and dissolved in the 5.0-ml. aliquot of acetone solution. This ensures uniform distribution of the  $\gamma$ -hexadeuterobenzene hexachloride throughout the sample.

The solution is evaporated to dryness to remove the acetone, then 5 ml. of petroleum ether are added to the residue to de-oil the crude. It is triturated at room temperature and finally in an ice bath for at least 5 minutes and filtered at once. The filtrate, which contains all the oil constituents of the crude (chiefly heptachlorocyclohexane), is rejected. The solid filter cake is placed in a flask equipped with a condenser, and is refluxed with 15 ml. of



a. Bands due to petrolatum vehicle used in making absorption layers

iso-octane for about 10 minutes to dissolve all the more soluble alpha, gamma, and delta isomers. The amount of iso-octane used should be based on a ratio of 0.1 gram of de-oiled sample per ml. This ratio has to be adhered to if pure gamma isomer is to be obtained at the end of this isolation procedure.

After refluxing, the flask is stoppered, put on a mechanical shaker, and shaken for at least 2 hours at room temperature. The solution is filtered and the filtrate evaporated to dryness on a steam bath. The residue weight at this point is usually between 0.35 and 0.40 gram, and its gamma isomer content is between 55 and 60% as determined by direct infrared spectrophotometry. This residue is crystallized from a 90% ethylene glycol-10% water mixture (by volume) as follows. An amount of the latter "solvent" corresponding to 11 mg. of

residue weight per milliliter is used and the system is heated on a steam bath with vigorous mechanical stirring until the solids are completely dissolved. The hot solution is filtered, seeded with a tiny crystal of the gamma isomer, and allowed to crystallize at about 5°C., being stirred only occasionally over no more than a 4-hour period. If longer periods are allowed, undesirably large amounts of the alpha isomer will be found in the solid. The crystalline solid is filtered and washed on the filter, first with a little of the ethylene glycol solvent and then with water until all the glycol has been removed. The solid is dried at  $56^{\circ}$  C. for about 1 hour in vacuo.

This product should be essentially pure gamma isomer and should have a melting point with a range no greater than from 108° to 112° C. to be of acceptable purity for the subsequent infrared measurements. This melting point range has been found to correspond to the presence of from 1 to 2% of the alpha isomer. If the product obtained does not meet this purity requirement it may be satisfactorily purified by recrystallization from isopropanol in the ratio of 190 mg. of product per ml. in the usual manner—i.e., dissolved on the steam bath and allowed to crystallize at room temperature. In this manner about 60 mg. of pure gamma isomer are obtained for the final infrared isotope dilution measurement as described above.

Most of the operations involved in the foregoing isolation procedure are so carried out as to avoid the attainment of thermodynamic equilibria for, in fact, if such equilibria were to be established the isolation of the pure gamma isomer would be impossible. It is, therefore, essential that the above procedure be followed in every detail.

If assays for the beta and alpha isomers are desired, a method for their isolation will be required. For these isomers, however, isolation is far more simple, inasmuch as the insolubility of the beta isomer makes its isolation practically a matter of simple filtration, while the fact that the alpha isomer occurs to the extent of 65 to 70% in the usual chlorination crude makes its isolation equally simple.

#### COMPUTATION OF RESULTS

As for any tracer dilution assay, the desired numerical result is computed from an equation of the following form:

$$F\gamma = \frac{W\gamma_D \left(1 - f\gamma_D\right)}{W_s f\gamma_D}$$

where

 $F\gamma$  = fraction of gamma isomer in scales  $W\gamma_D$  = weight in mg. of added isotopic tracer  $W_{\bullet}$  = weight in mg. of sample containing  $W\gamma_D$  mg. of tracer - fraction of deutero isomer found in the isolated specime = fraction of deutero isomer found in the isolated specimen

There are several possible ways in which the  $1 - f\gamma_D$  and  $f\gamma_D$ terms in the above equation may be evaluated.

First, since  $1 - f\gamma_D$  is equal to  $f\gamma_P$  (the fraction of the protio isomer) and the technique makes it possible to determine  $f\gamma_D$ and  $f\gamma_P$  as independent measurements at 13.75 and 11.83 mu, those two values could be introduced, as observed, into the equa-tion and so a value for  $F\gamma$  computed. Secondly and thirdly, one might elect to use either the  $f\gamma_D$  or  $f\gamma_P$  values, obtaining the  $1 - f\gamma_D$  or  $1 - f\gamma_P$  values by simple subtraction, and thus evalu-ate  $F\gamma$ .

The selection of which of the three methods to use in order to obtain the greatest accuracy in the final result will, in general, depend upon a variety of circumstances associated with the nature of the impurity likely to be present in the isolated isotopically diluted specimen. Unless the isolated isotopically diluted specimen can be made entirely pure, it is very likely that the impurity will affect the infrared absorption at one wave length more than at another and consequently the most accurate value of  $F\gamma$  will be



a. Bands due to petrolatum vehicle used in making absorption layers

obtained from the absorption measurement made at the wave length least perturbed in an unfavorable direction by the presence of the impurity.

A careful study of the effect of small amounts (about 1% or less) of the alpha isomer has shown that the most accurate value of  $F\gamma$  is obtained through use of the observed  $f\gamma_P$  value only. This is to be expected in view of the fact that the simple dilution effect which the presence of, say, 1% of the alpha isomer would have at all wave lengths is partially compensated for at the 11.83-mu band by the significant absorption of the alpha isomer due to the overlap of the 11.67-mu alpha and the 11.83-mu gamma bands. There is no equivalent effect at the 13.75-mu deutero gamma isomer band, since the protio alpha isomer has no absorption band at all in this region. Even this method of computation does not give an entirely accurate value for  $F\gamma$ , as Table IV show.

The average deviation from the known values is about + 0.5 unit and is always positive, indicating that the optical density measured at 11.83 mu is too large, because of the overcompensation of the alpha dilution effect by the alpha absorption effect. The degree of overcompensation, however, is such that the error in the accuracy of the final result obtained in this manner is smaller than that obtained by the other two methods of computation.

Naturally, this somewhat arbitrary treatment can be avoided by sufficient purification of the isolated specimen, so that all three methods of computation would give results of equal accuracy, but the authors have found it impractical, in general, to recrystallize sufficiently to remove the last few tenths per cent of the alpha isomer. Instead they prefer to correct the final result by subtracting 0.5 unit.

The data in Table V illustrate the precision in the determination of the infrared optical density measurements. These measurements were made with a known mixture of the pure deutero and protio gamma isomers.

Thus it appears that the most accurate representation of the assays of this dilution method is expressed by the following:

Table IV. Analy	tical Results Obtained wi Mixtures <sup>a</sup>	th Known
Known Percentage of Gamma Isomer	Experimental Percentage of Gamma Isomer $F_{\gamma b}$	Difference
20.0	21.2	$^{+1.2}_{-1.1}$
20.0 15.1	20.1 15.1	+0.1 +0.0
12.0 12.0	12.7 12.0	+0.7 +0.0
$10.0 \\ 20.0$	$\begin{array}{c} 10.7\\ 21.1 \end{array}$	+0.7 +1.1

<sup>a</sup> In every case a mixture of all four common isomers was used containing 60 to 70% of the alpha isomer, 10% of the beta isomer, and 10% of the delta isomer.

b  $F\gamma$  values calculated using only observed  $f\gamma P$  values.

Table V. $f_{\gamma P}$ Value	Kepro for a	ducibility Known Gam	of Infra Mixture ma C <sub>6</sub> H <sub>6</sub> (	ared Cor Cls	Determi ntaining	nation o 60.2% o	f
Time	, Days	$f\gamma F$ 13.75	Pat $f_{1}$ 5 Mu 11.	γ <i>P</i> at 83 Μι	1 Average	Difference	a
			01	00 F	00.0	100	

1 2 3 8 9	61 60 60 60 60	$\begin{array}{c} 60.5 \\ 60 \\ 61.5 \\ 60.5 \\ 61 \end{array}$	60.8 60.0 60.8 60.3 60.5	+0.8 -0.2 -0.2 -0.2 -0.2
Mixture recrystallized from ethylene glycol-water sol- vent	61	60	60.5 A	+0.8 v. ±0.2
6 Computed from 13, 75 mm	for B. Walue			

<sup>a</sup> Computed from 13.75 mu  $f\gamma P$  values

## $F\gamma_{\rm true} = (F\gamma_{\rm obsd.} - 0.5) \pm 0.4$

Table VI presents the results obtained with actual commercial benzene hexachloride crudes. These data also illustrate the degree of precision attainable for the complete analytical procedure when used in assaying typical chlorination crudes. In some of these samples as much as 10 to 15% of oily impurities were known to be present. Moreover, satisfactory assays have been carried out with samples containing as little as about 5% of the gamma isomer.



a. Bands due to petrolatum vehicle used in making absorption layers

Table	VI.	Analysis	of	Crude	Benzene	Hexachlorides
	Cru	de			$F\gamma$	
1 2 3 4 5 6				$\begin{array}{c} 12.7, \\ 14.0, \\ 17.0, \\ 11.2, \\ 12.9, \\ 16.2, \end{array}$	12.8 14.5,13.7 17.0,17.6,1 11.4,11.8,1 12.9 16.4,16.0	6.9 1.8,11.4

### SUMMARY

A mass isotope dilution method has been developed for absolute determination of the gamma isomer and, in principle, for some of the other known isomers of benzene hexachloride in crude benzene chlorination products. In particular, the use of infrared spectrophotometry as a means of determining the extent of the mass isotope dilution has been described and its extension as a general absolute assay technique for the analysis of many different kinds of substances under a wide variety of conditions visualized.

In general, it would appear much easier to introduce deuterium into an organic molecule as a marking atom than practically any other kind of atom, the more so if the organic molecule in question cannot be synthesized by other than natural methods, for hydrogen exchange is of far more common occurrence and more easily achieved under sufficiently mild conditions than is true for other kinds of atoms. Because the introduction of deuterium into a molecule results, in general, in rather extensive changes in its infrared spectrum, it should always be possible to determine the extent of the deuterium isotope dilution by such means. Even under the most unfavorable conditions where other changes in the infrared spectrum are only trivial the presence of the C-D linear stretching vibration at about 4.5 mu, a region not generally interfered with by other types of vibrations, would provide a means of analysis. Moreover, for compounds whose solubility properties preclude the use of any otherwise usable solvent, one can use solids equally effectively (1, 13). Thus the combined general methods employed in this paper are of considerable scope and interest from the point of view of the absolute analysis of organic substances occurring in complex media. The use of the concept of isotope dilution in analysis is not new (15), but the specific use of infrared spectrophotometry in determining the mass isotope dilution in place of the older and more cumbersome combustion-density of water methods is believed to be substantially original (14).

Because impurities are without effect upon the accuracy of this method, its reliability is limited only by its precision, which is constant over practically the whole range of concentrations, and moreover, as the precision would appear necessarily superior to that attainable by direct infrared analysis, the isotope dilution method must take precedence over it and all other methods as a primary assay by which the reliability of other methods may be gaged.

#### ACKNOWLEDGMENT

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#### LITERATURE CITED

- (1) Barnes, R. B., Gore, R. C., Williams, E. F., Linsley, S. G., and Petersen, E. M., IND. ENG. CHEM., ANAL ED., **19**, 620 (1947). Bowen, C. V., private communication.
- (3) Bowman, P. I., Benedict, W. S., and Taylor, H. S., J. Am. Chem. Soc., 57, 960 (1935).
- Daasch, L. W., IND. ENG. CHEM., ANAL. ED., 19, 779 (1947). (4)
- (6) Heal, R. E., and Dunn, H. A., forthcoming publication.
  (6) Herzfeld, N., Ingold, C. K., and Poole, H. G., J. Chem. Soc., 1946, 326.
- Ingold, C. K., Raisen, C. G., and Wilson, C. L., Ibid., 1936, 915. (8) Kauer, K. C., Du Vall, R. S., and Alquist, F. N., Abstracts of Papers, 110th Meeting AM. CHEM. Soc., p. 52 I, 1946; Ind. Eng. Chem., 39, 1335 (1947).
- (9) Kauer, K. C., Du Vall, R. B., and Alquist, F. N., Ibid., 39, 1336 (1947)
- (10) Oetjen, R. A., Kao, C.-L., and Randall, H. M., Rev. Sci. Instruments, 13, 515 (1942).
- Rosenblum, C., private communication.
- Slade, R. E., Chemistry & Industry, 64, 314 (1945).
   Trenner, N. R., and Walker, R. W., forthcoming publication.
- (14) Walcher, W., Ergeb. Exakt. Naturw., 18, 155 (1939).
  (15) Weissberger, A., "Physical Methods of Organic Chemistry,"
- Vol. II, p. 1296, New York, Interscience Publishers, 1946. (16) Weldon, L. H. P., and Wilson, C. L., J. Chem. Soc., 1946, 237.

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# **A Flowmeter for High Temperature Gases**

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THE development and specification of pyrotechnic fuel mixtures during World War II gave rise to the need for a simple but fairly accurate method of measuring the instantaneous volume rate of gas evolved (2). The required apparatus consists essentially of a sharp-edged orifice fitted with a shielded thermocouple in a high velocity gas stream to permit the simultaneous measurement of hot gas temperature and pressure across the orifice. A baffle was provided to prevent the thermocouple from "seeing" the incandescent surface of the pyrotechnic mixture. This device came to be known as a volume tester.

#### APPARATUS

The device was constructed in several sizes. Figure 1 shows a cross section through a typical unit.

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The gas from the surface of the pyrotechnic mixture flows around the baffle plate and through the tube containing the This tube serves the dual purpose of imparting thermocouple. a relatively high velocity to the gas flowing by the thermo-couple and of shielding the latter from the cooler sides of the apparatus. The gases then exhaust through the orifice to the atmosphere. A pressure connection is provided in the side of the unit near the orifice, which is connected to a manometer or pressure gage. Chromel-alumel B. and S. gage 22 thermocouple wires were found satisfactory with gas temperatures approaching 2000°,F. All except the junction was coated with Sauereisen for protection. The calibration of the couple was checked at a known temperature after each one to three tests.

The fuel is ignited and temperature and pressure readings are taken at frequent intervals throughout the burning time.

#### CALCULATIONS

The relationship between pressure drop across the orifice and the weight rate of flow is given by the Equation (1, 3)