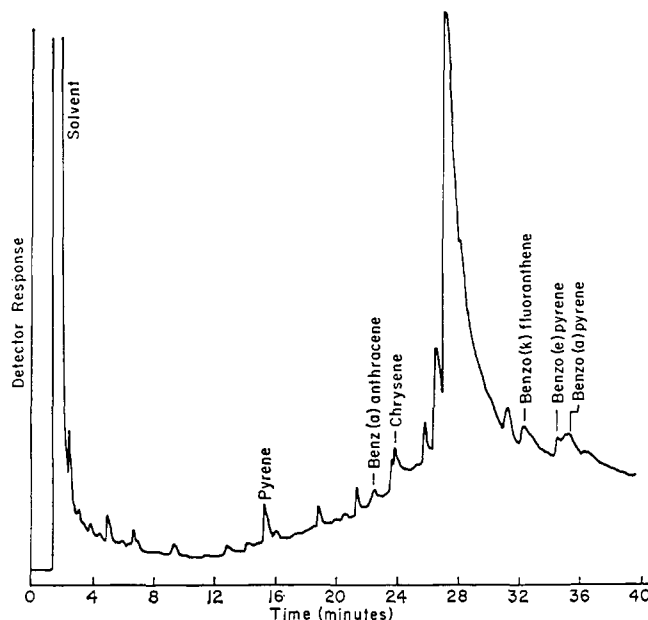


Figure 3. Chromatogram of a typical sample on SE-30



CONCLUSIONS

A method utilizing gas chromatography for the analysis of polynuclear aromatic hydrocarbons has been suggested for general use. The method was developed for use in analyzing polycyclic hydrocarbons associated with particulate matter in the air; however, it can be used wherever it is required to

analyze for polynuclear aromatic hydrocarbons.

The primary advantages of this method when compared to the methods now used are the ease of performance and time differential. One man can easily complete the analysis in two hours after the sample is extracted from the filter. Previously, several analysts required two days to complete the procedures.

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LAWRENCE DEMAIO
MORTON CORN

Graduate School of Public Health
University of Pittsburgh
Pittsburgh, Pa. 15213

WORK supported by funds contributed to the Graduate School of Public Health, University of Pittsburgh, by the Allegheny County Health Department.

Responses of Electron-Capture Detector to Halogenated Substances

SIR: Halogenated substances of certain types produce responses of great sensitivity in the electron-capture detector. In his early work, Lovelock reported responses for selected halogenated substances (3). Subsequently, much work has been done applying electron-capture techniques to the analysis of chlorinated types of pesticides; however, relatively few data are available on the experimental responses of lower molecular weight halogenated substances. Here responses have been measured for a considerable number of halogenated organic substances containing one to six carbon atoms and for several inorganic halogen-containing compounds. The substances contained fluorine, chlorine, bromine, and iodine atoms; a number contained two or three different halogen atoms. The responses varied over at least seven orders of magnitude. The responses of certain of these substances to the electron-capture detector will be compared to those obtained with the flame-ionization detector.

EXPERIMENTAL

Apparatus. A Model 2500 Micro-Tek dual-column gas chromatograph was equipped with an electron-capture detector mounted in parallel with a flame detector by use of a column effluent splitter. The electron-capture detector was a Micro-Tek detector with a 300-mc. tritium source substituted for a conventional 130-mc. source. The detector was equipped with a heater and with various controls for maintaining sample and scavenger flows; this arrangement allowed maximum versatility in studying the effects of various parameters. A Micro-Tek polarization voltage supply modified to provide 0 to 50 volts d.c. calibrated in 0.05-volt increments was used to apply a potential across the detector; a Gyra Model E-302 electrometer completed the assembly. The system was mounted to provide easy access to each component and was connected to allow measurement of either the standing current or a specific response, as required. The outputs from the two detectors were recorded on separate 0- to 1-mv. potentiometric records hav-

ing 1-second responses. All responses were brought to a common electrometer scale of 1×10^{-9} ampere and the base widths for all areas were computed at a chart speed of 2 inches/minute.

The prepurified nitrogen that served as the carrier gas, the prepurified hydrogen, and the air supply for the flame ionization detector were passed through a molecular sieve to remove water and other impurities. The flow rate to the electron-capture detector was 90 cc./minute, and the detector was maintained at 100° C. Polarization voltage of 11 to 14 volts was based on the optimization of response from the measurements on sulfur hexafluoride and bromotrifluoromethane. Sampling volume was 0.3 cc.

Chemicals. Many of the halogenated substances were obtained from the usual sources of Freons and other common halogenated substances. Samples of CBrF_3 , CBrF_2 , and $\text{IF}_3\text{C}-\text{CF}_2\text{I}$ were provided by Du Pont. Samples of CF_3Br_2 and $\text{CF}_3\text{CF}_2\text{CF}_2\text{I}$ were obtained from K & K Chemicals. Imperial Chemicals provided the three $\text{SF}_5(\text{CF}_2)_n\text{Cl}$ telomers. Halocarbons Products Corp. supplied unsaturated

halogenated substances. The SOF_2 and SOFCl were obtained from Pennsalt Chemicals Corp.

A column of 80- to 100-mesh Baymal (1) (a colloidal alumina), $\frac{1}{8}$ -inch o.d. and 8 feet long, was used for low molecular weight Freons; a column of 10% SF-96 on 50- to 60-mesh siliconized Sil-O-Cel C-22 firebrick, $\frac{1}{8}$ -inch o.d. and 12 feet long, was used for the more polar Freons and other highly polar materials.

Figure 1 illustrates the method finally selected for preparing dilute vapor concentrations in nitrogen. Because a large number of samples was involved, a rapid method of preparing known concentrations was required. The dry test meter and other parts of the apparatus were selected to allow minimum resistance at rapid flow through the system. The system allows a sample dilution of 250,000,000 to 1 when 1 $\mu\text{l.}$ of gas is diluted with 250 liters of nitrogen. The limiting factor is the precision with which the sample is measured and injected. Further dilution can be achieved by use of a second container to

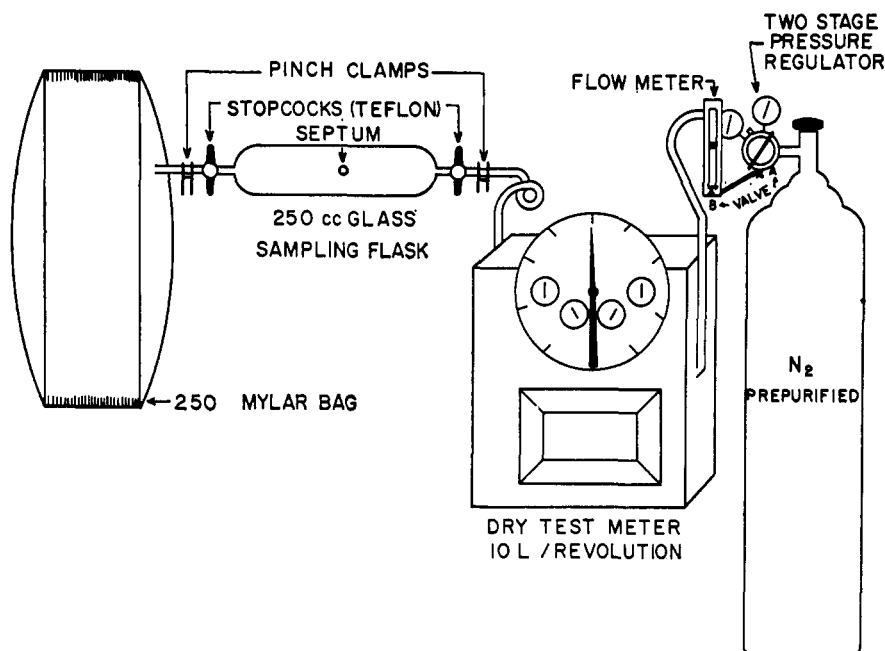


Figure 1. Diagram of apparatus for preparing known concentrations of vapors

Table I. Responses of the Electron-Capture Detector to Various Halogenated Compounds

Compound	Test concn., p.p.m.	Response, sq. in. p.p.m.
CHF_3^a	4000	$<10^{-4}$
CF_4^a	4000	3×10^{-4}
$\text{CH}_3\text{CHF}_2^b$	20	9×10^{-3}
$\text{CF}_3\text{CF}_2\text{CF}_3^a$	4000	3×10^{-4}
$\text{CF}_3\text{CF}=\text{CFCF}_3^b$	0.4	40
$(\text{CF}_3)_2\text{C}=\text{CF}_2^b$	0.02	90
$\text{CF}_2=\text{CF}_2-\text{CF}_2-\text{CF}_2^b, c$	0.02	30, 40
$(\text{CF}_3)_2-\text{CF}_2-\text{CF}_2-\text{CF}_2\text{CF}_2^c$	0.013	90
CHF_2Cl^b	20	3×10^{-3}
CF_3Cl^c	4000	1×10^{-3}
$\text{CF}_3\text{CF}_2\text{Cl}^b$	20	5×10^{-2}
$\text{CF}_2=\text{CFCl}^b$	15	3×10^{-2}
CHFCl_2^b	20	5×10^{-2}
CF_2Cl_2^c	0.5	9
$\text{ClF}_2\text{C}-\text{CF}_2\text{Cl}^b$	0.5	2
$\text{CF}_2=\text{CCl}_2^b$	0.04	0.2
CHCl_3^c	0.06	10
CFCl_3^c	0.004	370
$\text{ClF}_2\text{C}-\text{CFCl}_2^c$	0.05	50
$\text{ClHC}=\text{CCl}_2^c$	0.04	20
CCl_4^c	0.005	650
$\text{CF}_3\text{Br}^a, b$	0.03	40, 12
$\text{F}_3\text{C}-\text{CHClBr}^c$	0.017	120
CH_2Br_2^c	0.02	300
CF_2Br_2^b	0.01	500
$\text{BrF}_2\text{C}-\text{CF}_2\text{Br}^c$	0.009	230
$\text{CF}_3\text{CF}_2\text{CF}_2\text{I}^c$	0.007	180
$\text{IF}_2\text{C}-\text{CF}_2\text{I}^c$	0.004	1200
C_6F_6^c	0.42	1000
SF_6^a	0.003	580
$\text{SF}_6(\text{CF}_2)_2\text{Cl}^c$	0.002	520
$\text{SF}_6(\text{CF}_2)_4\text{Cl}^c$	0.005	430
$\text{SF}_6(\text{CF}_2)_6\text{Cl}^c$	0.004	460
SOF_2^b	0.25	5
SOFCl^b	0.5	0.2

^a Baymal column at 65° C. ^b SF-96 column at 30° C. ^c SF-96 column at 65° C.

hold a primary dilution; an appropriate sample can be withdrawn from the container and injected into the system for further dilutions.

Procedure. A sample of known concentration is prepared and analyzed by flushing an appropriate syringe with the compound of interest and injecting a given quantity through the septum into the closed gas-sampling flask. The sample is then flushed into an evacuated Mylar bag by opening the stopcocks (Teflon) on the flask and subsequently opening toggle valve A to allow nitrogen to flow through the dry test meter and into the bag. The volume of nitrogen passed to the bag is determined by closing the valve and noting the quantity passed as recorded by the meter. A calculation is then made to determine the final sample concentration. Contamination of the meter is prevented by passing only prepurified nitrogen through the meter and by rigorously limiting the use of the meter to this one application.

Samples are allowed 1 hour to reach vapor equilibrium before being connected to the sample inlet of a gas sample valve. Vacuum is then applied and sample drawn through the calibrated loop at a rate of 100 to 200 ml./minute. The vacuum is removed and the sample is injected into the chromatograph by depressing a plunger on the gas sample valve.

Because of the nature of the study it was desirable to determine the degree of homogeneity of the gas mixtures at various time intervals up to several hours. Measurements also were made to determine possible losses due to adsorption of the trace substances on the plastic film.

Homogeneity of the contents of the bags was determined by following the

response at intervals of 15 minutes for about 2 hours. After 15 minutes most of the vapor concentrations had reached equilibrium and little if any increase in response could be noted after 30 minutes. Manual kneading of the bags did little to speed the process.

Possible losses were determined by evacuating the bags and partially refilling with about 40 liters of nitrogen, waiting an appropriate interval, and analyzing for desorbed vapor in the nitrogen. Residual amounts of compounds such as SF_6 could not be detected after such a manipulation. For CBr_2F_2 initially at 0.01 p.p.m. such treatment resulted in 2.7% desorbed vapor. This represents an extreme case because CBr_2F_2 is one of the heaviest materials used. Residue values were considerably lower for other materials.

Responses of the electron-capture detector are summarized in Table I. The peak areas per p.p.m. by volume are plotted on a log scale in Table II for the more sensitive substances. The response values are compared for convenience in units of area per p.p.m.; they should not be interpreted as indicating linearity in response over any particular concentration range.

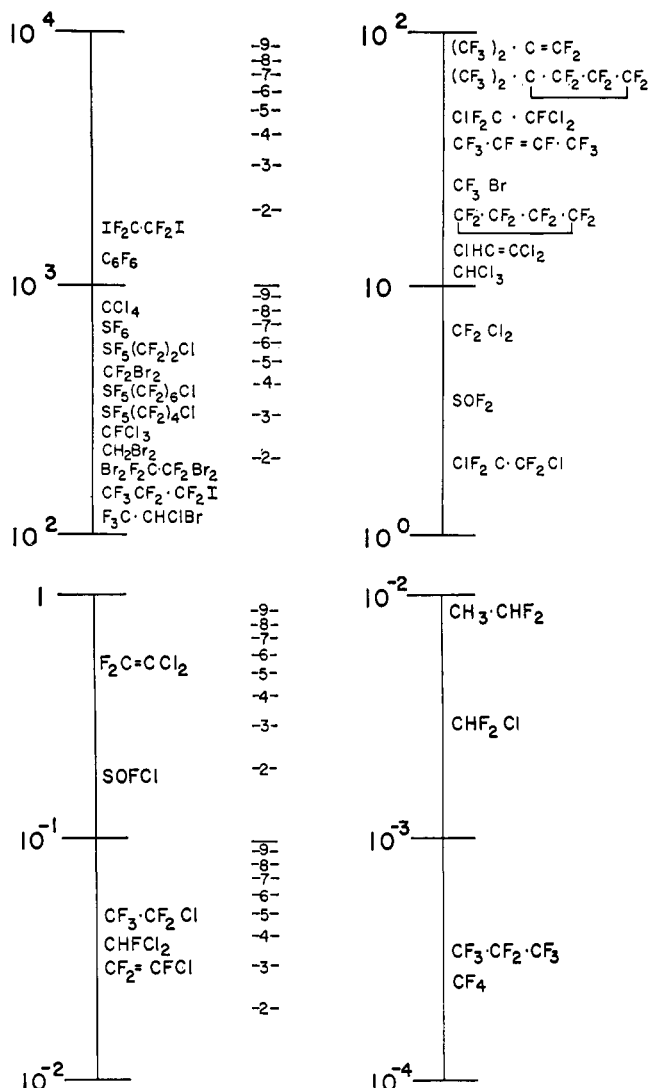
RESULTS AND DISCUSSION

The responses varied over about seven orders of magnitude. Low responses are shown by saturated and vinyl-type fluorinated hydrocarbons including those containing one chlorine atom. Compounds with the chlorine atom attached to a vinyl carbon gave lower responses than the corresponding saturated compounds. Attachment of the chlorine to an allyl carbon atom resulted in greater sensitivity than that obtained for the corresponding saturated compound. The response characteristics of the fluorinated cyclobutane ring closely resembled those of compounds with allyl CF_3 groups. The completely fluorinated benzene derivative, C_6F_6 , gave a high response. As Lovelock and Gregory reported previously (3), the response decreased in the order $\text{I} > \text{Br} > \text{Cl} > \text{F}$ and also increased markedly with increase in the number of Cl, Br, or I atoms in the molecule. One iodine atom in a molecule caused about the same response in the same range as two bromine atoms or three chlorine atoms. Responses in molecules of different structures containing the same number of halogen atoms varied by one to two orders of magnitude. Landowne and Lipsky also observed that responses varied by one to two orders of magnitude for the isomeric butyl chlorides, bromides, and iodides (2). While SF_6 and its telomers $\text{SF}_3(\text{CF}_2)_n\text{Cl}$ gave high responses, the corresponding SO_2X_2 compounds have much lower sensitivities.

In a later experiment measurements were made on several cyclic and aromatic compounds. Relative to hexafluoro-

Table II. Range of Response of Survey Compounds (Log Scale)

(Sq. inch/p.p.m.)



benzene, pentafluorobenzene was less sensitive by a factor of 10^2 . Perfluoromethyl cyclohexane, however, gave a response about equal to that of hexafluorobenzene.

As discussed by Landowne and Lipsky (2) and Lovelock and Gregory (3), electron-capture attachment can occur by two processes including $\text{RX} + e^- \rightarrow [\text{RX}]^- \rightarrow \text{R} \cdot + \text{X}^-$. The variations in response of compounds with equal numbers of halogen atoms indicates the importance of the stability of the R radical. Note the similarity of reactivity characteristics in this type of process and in the reaction $\text{RX} + \text{Na} \rightarrow \text{R} \cdot + \text{NaX}$ studied by Polanyi and co-workers and reviewed by Warhurst (4). The collision yields for these reactions vary by 10^6 for the methyl halides in the order of reactivities $\text{I} > \text{Br} > \text{Cl} > \text{F}$. Similarly the re-

activities for this reaction decrease by a factor of 400 in the order $\text{Cl}_4 > \text{Cl}_3 > \text{Cl}_2 > \text{Cl}$. The reactivities of the allyl and benzyl derivatives are greater than those of the corresponding saturated compounds, while those of the vinyl derivatives are less. Thus, gas phase reaction of RX with the electron-donating sodium atom has many similarities to the reaction of RX with the electron.

Of interest is the minimum amount of a high-response substance, such as SF_6 , that is detectable with the instrumentation described. A 0.3-cc. sample containing 0.0033 p.p.m. of SF_6 causes 165 units of recorder response. If it is assumed that noise is 1 unit and that detection occurs at a 2 to 1 signal-to-noise level and a 20-fold increase in sample size, it should be possible to detect 10^{-12} part of SF_6 in the sample. With concentration techniques, several

orders of magnitude of additional sensitivity should be readily accessible.

The response of the flame-ionization detector falls in the range of about 0.1 to 1 square inch/p.p.m. Thus, the flame-ionization response of compounds such as CHF_2Cl , $\text{CF}_3\text{ClCF}_2\text{CF}_2\text{Cl}$, $\text{CH}_2=\text{CF}_2$, CH_3CHF_2 , and even some of the dichloro derivatives such as CHFC_2Cl or $\text{CF}_2=\text{CCl}_2$ are 10 to 1000 times greater than their electron-capture responses. For other compounds containing two chlorine atoms, and for compounds containing three or more chlorine, bromine, or iodine atoms, the electron-capture response is much greater than the flame-ionization response. If sensitivity is the major consideration, the flame-ionization detector has a place even in the analyses

for many halogenated substances. If specificity is critical, the greater specificity of the electron-capture detector may favor its use even for halogenated substances showing low responses to this detector.

ACKNOWLEDGMENT

We acknowledge the assistance of Andrew E. O'Keeffe, who procured many of the compounds and suggested several worthwhile approaches to the many problems encountered, and of Arthur I. Coleman, who assisted in obtaining the data on relative responses.

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C. A. CLEMONS
A. P. ALTSHULLER

Laboratory of Engineering and Physical Sciences, Division of Air Pollution
Robert A. Taft Sanitary Engineering Center, Public Health Service
U. S. Department of Health, Education, and Welfare
Cincinnati, Ohio 45226

PRESENTED before the Division of Water, Air, and Waste Chemistry, 148th Meeting, American Chemical Society, Chicago, Ill., September 1964. Mention of commercial products does not constitute endorsement of the Public Health Service.

Reaction Rate Measurements with Cation-Sensitive Glass Electrodes

A Kinetic Study of Some Tetraphenylborate Precipitation Reactions

SIR: Although cation-sensitive glass electrodes have been used for a variety of chemical measurements (15), they have not yet been employed in rate or kinetic studies. Such electrodes accurately and selectively monitor ion activities in solution, however, and should also be effective in following the appearance or disappearance of appropriate ionic species in the course of chemical reactions. It may be expected that the range of application of glass electrodes to kinetic studies will be limited not only by selectivity and sensitivity considerations but also, in the case of fast reactions, by the finite response times of such electrodes. In this paper, we report on the use of cation-sensitive glass electrodes in the study of the kinetics of several precipitation reactions involving univalent cations and tetraphenylborate. The utility of such measurements is extended to fast reactions through the use of a rapid-mixing flow technique (1) of a kind similar to that described by Roughton and Chance (17) which employs a pH-type glass electrode.

Tetraphenylborate precipitation reactions were chosen for this study because of the great importance of such reactions to chemical analysis (5) and because of the demanding requirements of heterogeneous reaction rate measurements.

While crystallization and precipitation reactions have received the attention of many workers (11), precipitation kinetics are by no means as well understood as are homogeneous solution reactions. A variety of techniques (10), including light scattering, interferometry, potentiometry, conductometry,

and polarography, have been used to follow precipitation reactions. Tetraphenylborate precipitations of NH_4^+ , K^+ , Rb^+ , Cs^+ , Tl^+ , or Ag^+ have not previously been considered from the kinetic viewpoint.

EXPERIMENTAL

Apparatus. The experimental arrangement devised to follow fast precipitation reactions is shown in Figure 1. The mixing chamber consisted of a three-way, T-shaped stopcock (1-mm. diameter bore) and was fed, with the two reactant solutions, from a reservoir under nitrogen pressure and a Radiometer Type ABU 1a Auto Burette, respectively. The indicator electrodes were Beckman Model 39047 cation-sensitive glass electrodes and were inserted by ground glass joint into a Beckman Model 46850 microflow assembly which was attached to the outlet of the mixing chamber. A Beckman Research Model pH meter was used to amplify the electrode response, which was displayed as a function of time on a Photovolt Model 43 recorder. The slower precipitation reactions were monitored directly in an open vessel, using the glass electrode and saturated calomel reference electrode, after rapid mixing of the two reagent solutions.

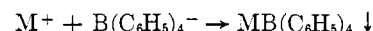
Reagents. A buffer solution, consisting of 0.1M tris(hydroxymethyl)aminomethane (THAM)—Fisher Primary Standard—and 0.01M acetic acid was prepared by adjusting the pH to 5.1 with G. F. Smith reagent grade HClO_4 and was used as the solvent in all experiments.

Cesium and rubidium stock solutions were prepared from the chloride salts obtained from Fisher Scientific Company. Thallium(I) solutions were prepared by dissolving Tl_2CO_3 (A. D. Mac-

kay, Inc.) in HClO_4 . Baker reagent grade NH_4Cl , AgNO_3 , and KCl were used for preparing NH_4^+ , Ag^+ , and K^+ solutions.

Calcium tetraphenylborate was prepared from Fisher Scientific reagent grade $\text{NaB}(\text{C}_6\text{H}_5)_4$, according to the procedure of Rechnitz, Katz, and Zamochnick (16), and was standardized by potentiometric titration with KCl and RbCl . A solution of calcium tetraphenylborate dissolved in the buffer medium served as a source of tetraphenylborate ion in all experiments.

Procedure. The precipitation rates of NH_4^+ , K^+ , and Rb^+ with tetraphenylborate ion were followed directly with a cation-sensitive glass electrode which had been preconditioned in a buffered $10^{-3}M$ solution of the metal ion to be studied for at least 24 hours. The reaction vessel initially contained about 20 ml. of a solution of the metal ion (M^+) in a THAM buffer (pH = 5.1). The required volume of $\sim 0.15 F$ $\text{Ca}[\text{B}(\text{C}_6\text{H}_5)_4]_2$ was injected into the stirred solution, and the potential of the cation-sensitive glass electrode vs. SCE was recorded as a function of time. Millivolt readings were then converted into M^+ concentration values (from a $\log M^+$ vs. millivolt calibration curve); and, with known stoichiometry of reaction between $\text{B}(\text{C}_6\text{H}_5)_4^-$ and M^+ (5), the $\text{B}(\text{C}_6\text{H}_5)_4^-$ concentration corresponding to each M^+ concentration was calculated. This procedure was repeated for several different initial concentrations of $\text{B}(\text{C}_6\text{H}_5)_4^-$ and M^+ in an attempt to obtain information leading to the mechanism of the overall reaction



All experiments were carried out at $24.8^\circ \pm 0.3^\circ \text{C}$.

Since Cs^+ , Tl^+ , and Ag^+ react too rapidly with $\text{B}(\text{C}_6\text{H}_5)_4^-$ to allow meas-