Hyg. Assoc. J. 47(1):27-36 (1986)

Evaluation of an ISO Draft Proposal for Sampling and Analysis of Chlorinated Hydrocarbon Solvent Vapors in Workplace Atmospheres

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The ISO draft proposal for sampling and analysis of chlorinated hydrocarbon solvent vapors in workplace atmospheres (ISO/TC 146/SC 2/WG4 N41) has been evaluated by means of a round-robin test. For this purpose, the repeatability and reproducibility for the determination of tetrachloromethane, trichloromethane, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene were determined at three concentration levels. Furthermore, parameters such as breakthrough and loss on storage were determined. Samples were taken by 11 participants from six countries. After statistical evaluation of the results, it appeared that improvements were necessary for the determination of tetrachloromethane and trichloromethane. For the other three compounds, repeatability and reproducibility were sufficient. Possible error sources and possibilities for improvements are discussed.

Introduction

Chlorinated hydrocarbons are widely applied as solvents. Degreasing in the metal industry, industrial textile cleaning, and solvents in the paint industry are just some examples.

The discovery of the neurotoxic character and suspected carcinogenicity of several of the aliphatic chlorinated hydrocarbons[1] has resulted in a steady lowering of the acceptable concentration limits of these compounds in the workplace atmosphere in a number of countries. In order to increase the reliability of measurement of chlorinated hydro-carbon solvent vapors, the ISO has drafted a proposal for sampling and analysis of chlorinated hydrocarbon solvent vapors in workplace atmospheres.[2] An international round-robin test was organized by the TNO Research Institute for Environmental Hygiene for the evaluation of this draft proposal. The results of the round-robin test are described in this paper.

Summary of the ISO Proposal

The proposal is designed to be suitable for the following compounds:

- dichloromethane
- trichloromethane
- tetrachloromethane
- 1,1-dichloroethane
- 1,2-dichloroethane
- 1,1-dichloroethene
- 1,2-dichloroethene
- 1,1,1-trichloroethane
- 1,1,2-trichloroethane
- trichloroethene
- 1,1,2,2-tetrachloroethane
- tetrachloroethene
- 1,2-dichloropropane
- chlorobenzene
- 1,2-dichlorobenzene.

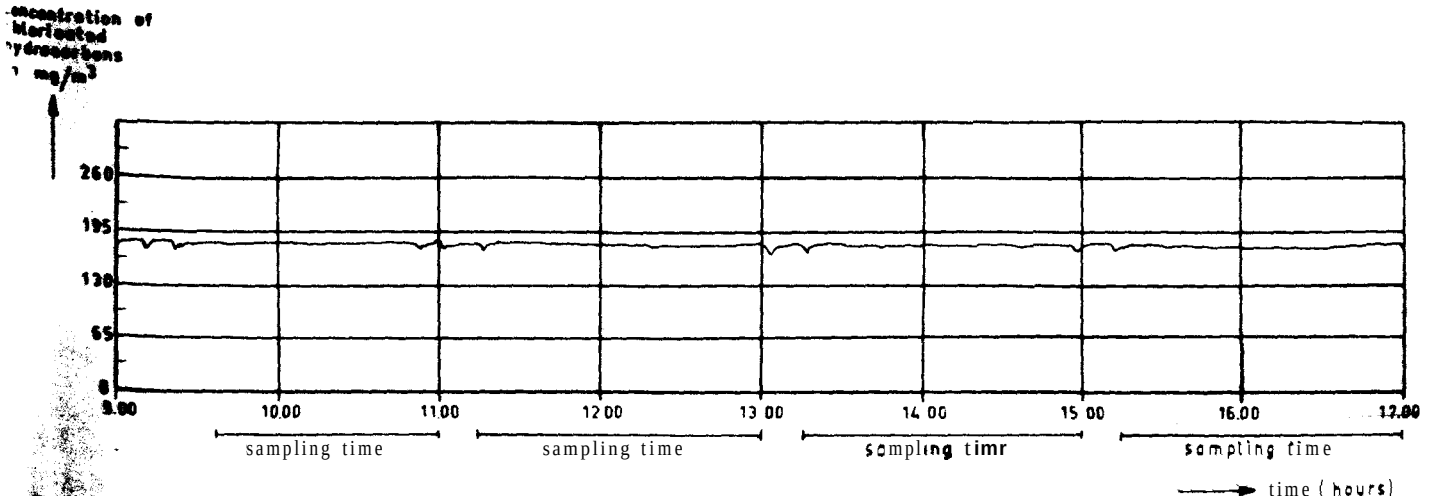


FIGURE 1—Concentration of chlorinated hydrocarbons *vs* time (recorded with MIRAN® 1A gas analyzer). Date. 30 May 1983.

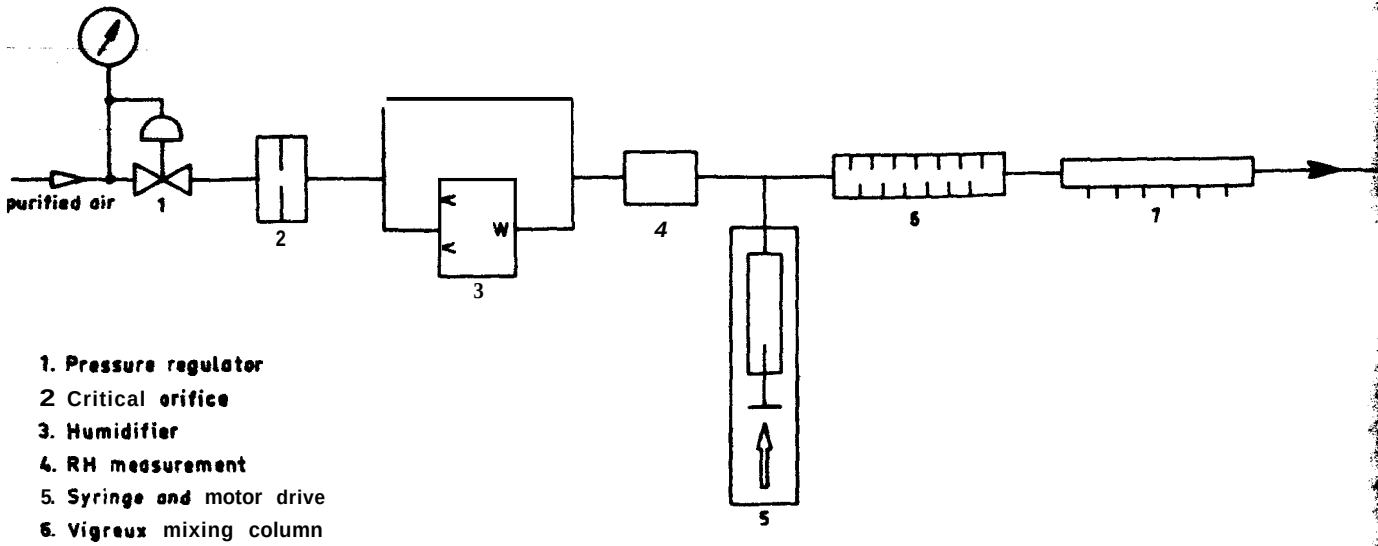


Figure 2—Preparation of known concentrations of chlorinated hydrocarbon solvent vapors in air.

The method described is a pumped charcoal tube-solvent desorption gas chromatographic method. A known volume of air is drawn through a glass or metal tube by means of a sampling pump; 1 g of activated coconut charcoal appears to be necessary for the adsorption of the chlorinated hydrocarbon vapors in the concentration range of interest. The organic vapors collected are desorbed by a suitable solvent and analyzed by means of gas chromatography with flame ionization detection. The peak heights or peak areas are compared to those of standard solutions in carbon disulphide. Breakthrough is determined in each sample by means of a back-up section in the tube. Desorption efficiencieshave to be determined for each lot of tubes by preparation of spiked samples on charcoal.

The proposal is fully described in reference.[2]

General Procedure of the Experiment

In the ISO draft proposal 15 compounds are listed to which the proposal is meant to be applicable. As it was not possible to test all 15 compounds in one run, 5 of them were selected for the test, namely. tetrachloromethane, trichloromethane, 1, 1, 1-trichloroethane, trichloroethene, and tetrachloroethene.

All participants took samples simultaneously in duplicate from a common sampling manifold in which a test atmosphere with a constant concentration of a known fixed mixture of the chlorinated hydrocarbons to be tested was maintained. The test atmosphere was generated dynamically, the flow available being at least fivefold in excess relative to the test gas consumption due to sampling.

Three concentration levels for each mixture were established on subsequent days. The relative humidity of the test atmosphere was 50±2%. Each participant took eight samples (four duplicates) of each concentration level — four in the morning and four in the afternoon. The sampling time of each sample was 90 min at a flow rate of about 0.1 L/min, resulting in a total volume of about 9 L per sample. The samples were analyzed at the laboratories of the participants. The desorption efficiency of each component also determined by the participants themselves.

The results were evaluated statistically according to ISO International Standard 5725.[3]

Description of the Test Gas Atmosphere Generator

Test gas mixtures with known concentrations of the chlorinated hydrocarbons of interest were generated by a dynamic volumetric method using the continuous (syringe) injection technique.[4] A diagram of the test gas generator is presented in Figure 1.

Zero test gas was prepared by purification of compressed air. The air was cleaned in a filter system consisting of a filter, a heatless dryer, a section of a molecular sieve 13X and an absolute filter. The purified air contained less than 1 ppm of water vapor. and the concentrations of the individual chlorinated hydrocarbons were below 0.1 ppb.

Zero test gas was humidified by passing an adjustable part of it through a thermostatically controlled bubble flask containing distilled demineralized water and mixing the water vapor-saturated part again with the dry part of the zero gas. The relative humidity was monitored continuously and registered. On each of the test days, the relative humidity was ± 2%.

Gravimetrically prepared mixtures of the chlorinated hydrocarbons were injected directly into the humidified air stream (12-18 L/min) by a motor driven syringe pump. In order to diminish concentration fluctuations due to irregular rate of evaporation, the capillary tube of the syringe was fitted into a quartz fiber filter fixed in the stream of zero gas.

Fresh mixtures of the liquid components were prepared each day. The chemicals were of reagent grade quality. The syringes used had a volume of 100 mL for the high and middle concentration levels and a volume of 20 mL for the lower concentration level. The capacity of these syringes was sufficient for the production of the test atmosphere

TABLE I
Homogeneity of the Test Gas Atmosphere and Reproducibility of the Determination

Analyte	Concentration generated (mg/m³)	Concentration determined (mg/m³)	R.S.D. (95% level) %
trichloromethane	113.0	117	5.4
	667.0	655	3.8
tetrachloromethane	22.5	22	7.4
	132.0	130	3.2
1,1,1-trichloroethane	864.0	908	5.2
	5086.0	5086	4.2
trichloroethene	179.0	185	5.0
	1056.0	1032	4.6
tetrachloroethene	286.0	296	4.0
	1685.0	1586	4.8

The quantity of the component mixture supplied mined by weighing the syringe. In addition, the ation of the chlorinated hydrocarbons (lumped monitored continuously by near infrared spectros- method afforded the possibility of accurate calcu- the composition of the test atmosphere during each period.

rate of the zero test gas was controlled by a lator and critical orifice combination. The flow to calculate the final concentration were meas- mercury-sealed piston flowmeter, equipped with electronic timer to measure the time of dis- the piston between two fixed sensors.

of the glass cylinder between the sensors was two methods.

relied on the displacement of air volume by a of oil. The other was based on the determi- loss of mass of a cylinder with compressed a preweighed cylinder. a constant flow was was measured periodically by the volumeter time. From the loss of mass of the cylinder and flow rate was calculated and the volume two detector marks was determined. The esti- racy in the volume determination is 0.3%.

Duplicate measurements of the flow rate (beginning and end of each test day) were within 0.2%.

The repeatability of the determination of the quantity of the liquid metered had been determined before performance of the test and appeared to be 0.002% at the lowest concentration level, 0.006% at the middle level and 0.03% at the highest level (95% confidence interval, mean of ten determinations). The total error estimate expressed as the root sum of squares of all errors — assuming these are independent — is 1% at the 95% confidence level.

Constancy and Homogeneity of the Composition of tbt Test Gas Atmosphere

Slight fluctuations in the composition of the test gas atmosphere may occur by fluctuations in the gas stream or in the injection system, or by irregularities during the evaporation of the injected liquids (the description of the test gas atmosphere generator). The constancy of the gas concentration is determined by means of infrared spectrometry and has been found to be better than 5% for all concentration ranges during the sampling periods (Figure 2). The volume of the test installation is 2 L. The gas flow being 20 L/min and the sampling time 90 min, the discrepancy in the composition of the samples which are taken simultaneously due to fluctuations of the gas mixture composition will be at most 0.005%.

TABLE II
Round-Robin Test for Chlorinated Hydrocarbons Sampling Equipment

Participant number	Sampling pump		Charcoal tube		Flow control[A]
	manufacturer	type	manufacturer	lot no.	
1	Compur	4903	SKC	120	s
2	DuPont	P125A/P200	SKC	120	s
3	MDA	808	SKC	120	s
4	Sipin	SP15	SKC	120	s,w
5	DuPont	S200	SKC	120	s
6	DuPont	P125	SKC	120	s
7	DuPont	P4000	SKC	120	w
8	DuPont	P4000	Supelco	459641	w
9	Sipin	SP1	SKC	120	s
10	DuPont	P4000	Dräger B		s
11	DuPont	P4000	SKC	120	s

[A] s = soap bubble tube
w = water displacement gas meter

The homogeneity of the gas mixture and the reproducibility of the determination have been investigated by taking five samples from different positions of the test installation. The results are summarized in Table 1. The reproducibility falls within the limits calculated in the Results Section.

Performance of the Test

The participating laboratories are listed below in alphabetic order.

•Akzo Corporate Research	Arnhem	Nederland
•Allgemeine Versicherungsanstalt	Wien	Osterreich
•Berufsgenossenschaftliches Institut fur Arbeitssicherheit	Sankt Augustin	Bundesrepublik Deutschland
•Centrilab	Soest	Nederland
•Directoraat-Generaal van de Arbeid	Voorburg	Nederland
•DSM-Research and Patents	Geleen	Nederland
*Health and Safety Executive	London	England
•IMG—TNO	Delft	Nederland
•INRS	Vandoeuvre	France
•NIOSH	Cincinnati	U S.A.
•Shell Nederland Chemie B.V.	Rotterdam	Nederland

in all other Tables the participants are represented by a random number.

The participants used their own sampling and calibration equipment. Analyses were performed on different gas chromatographic (GC) columns. The equipment used and the dates of analysis are summarized in Tables II and 111.

Sampling was carried out according to Paragraph 7 of the proposal.[11] The sampling rate was 100 mL per minute and the sampling time amounted to 100 minutes. Each participant took eight samples per day (four duplicate samples). in this way 88 samples were collected from each concentration range. The sample tubes were transported and stored at a temperature of -20° C or less. Gas chromatographic a... preparation of the calibration curve and deter... the desorption efficiency were carried ... Paragraph 8 of the proposal.[11]

Results

Results of Analysis

Graphic representations of the results of analysis ... samples are presented in Figures 3 to 7. About 10% ... results appeared to be missing, mostly because the cha... tubes had not been loaded with any material at all. A... reason for unsuccessful samples was breakage of the ... coal tubes or vials during workup of the samples.

Desorption Efficiency (DE)

Desorption efficiencies reported by the participan... presented in Table IV. Desorption efficiencies were ... mined according to Paragraph 8.3 of the propos... alternative method described in Annex C was not u...

Breakthrough

Preliminary breakthrough experiments were carri... before performance of the round-robin test with c... tubes containing 100 + 50 mg of coconut charcoal a... taining 800 + 200 mg of coconut charcoal in the fro... back-up sections, respectively. The specifications ... tubes met those prescribed in Paragraph 5.2.1. ... proposal.

The experiments were performed with the highest ... trations of analytes to be used in the round-robin ... lative humidity used in all experiments was 50 ± 2... ISO-proposal, a method for the determination of th...

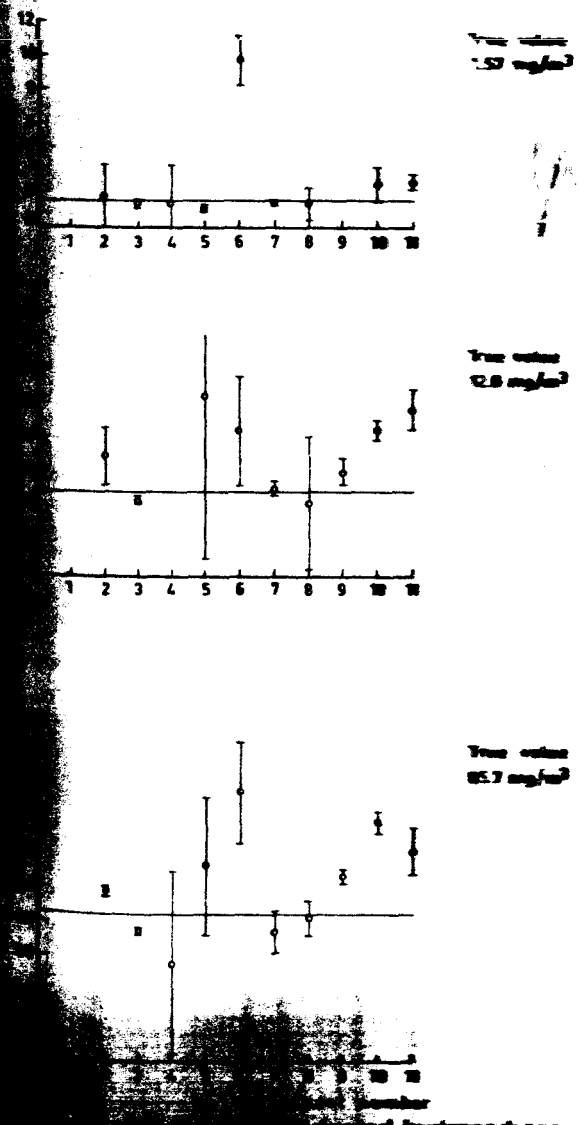
TABLE III
Round-Robin Test for Chlorinated Hydrocarbons
Analysis Equipment and Dates of Analysis

Participant number	Gas chromatograph manufacturer	type	Chromatography column stat. phase	length	I.D.	Detector	Time between sampling and analysis (weeks)
1	Packard Becker	GC433	[B]			FID	[A]
2	Varian	3700	SE-30	40.0 m	0.28 mm	FID	2
3	Packard	429	CPsil 5 CB	50.0 m	0.32 mm	FID	1-2
4	H.P.	5880	SE-54	25.0 m	0.32 mm	FID	3
	Carle Erba	2900	OV101	25.0 m	0.32 mm	MPECD	
S	Perkin Elmer	Sigma 3B	CPsil 5	25.0 m	0.32 mm	FID	<1
6	Perkin Elmer	Sigma 1	20% SE-30 + 0.5% polypurgent	2.0 m	⅛ inch	FID	<1
7	H.P.	5840 A	SE-30	50.0 m	0.7 mm	FID	<1
8	H.P	5730 A	GP 20% SP2100/ 0.1% carbowax	53.0 m	1.2 mm	ECD	5-8
9	Perkin Elmer	F17	OV101	3.0 m	2.0 mm	FID	<1
10	Perkin Elmer	F22	OV101	50.0 m	0.25 mm	FID	<1
11	Intersmat	IGC120FL	SE-30	4.5 m	⅛ inch	FID	2-4

[A] = not specified
[B] = two separation methods have been u s d by this participant
Method 1: SE-30, 50 m, 0.25 mm ID
Method 2: MD55 Multidimensional Switching System
pre-column: SE-30 6m ⅛"
main-column: SE-30 35 m × 0.25 mm

...ne is prescribed (see Annex A of Reference 2), ...hich is based on a continuous registration of ... of the gas mixture flowing through the ... suitable only for the determination of the ...olume of single components. Because this ...t the breakthrough value of a number of ... mixture had to be determined, the method ... not appropriate. For this reason the ... method was chosen: different volumes were ...e front and back-up sections of the tube were ...wards.

...of these experiments, expressed as the percen... in the back-up section *vs* the total amount of ...isted in Table V. These results show that small ...es were not suitable for the round-robin test. ...son all preliminary experiments were performed ... mg charcoal tubes. In the round-robin test 1000 ...oal tubes were used as well. No breakthrough ...ted by the participants.



...hane. Mean values and ...ervals.

...hydrocarbons.

Statistical Evaluation of the Results

Criteria

The results were evaluated according to ISO 5725. The following tests are prescribed in this Standard.[4]

- Cochran's maximum variance test for the determination of repeatability.[5] In this test, the highest variance found is divided by the mean of the remaining variances and the resulting value is compared to a numerical criterion, depending on the number of replicates and the number of participants.
- Dixon's outliers test for the determination of reproducibility. In the Dixon test, the highest and the lowest result of the analyses found by the participants are compared to the remaining results. This means that, contrary to Cochran's test, Dixon's test is a two-sided one.

Repeatability and reproducibility are defined as follows.[5] The repeatability r is the value below which the absolute difference between two single test results obtained with the same method on identical test material. under the same

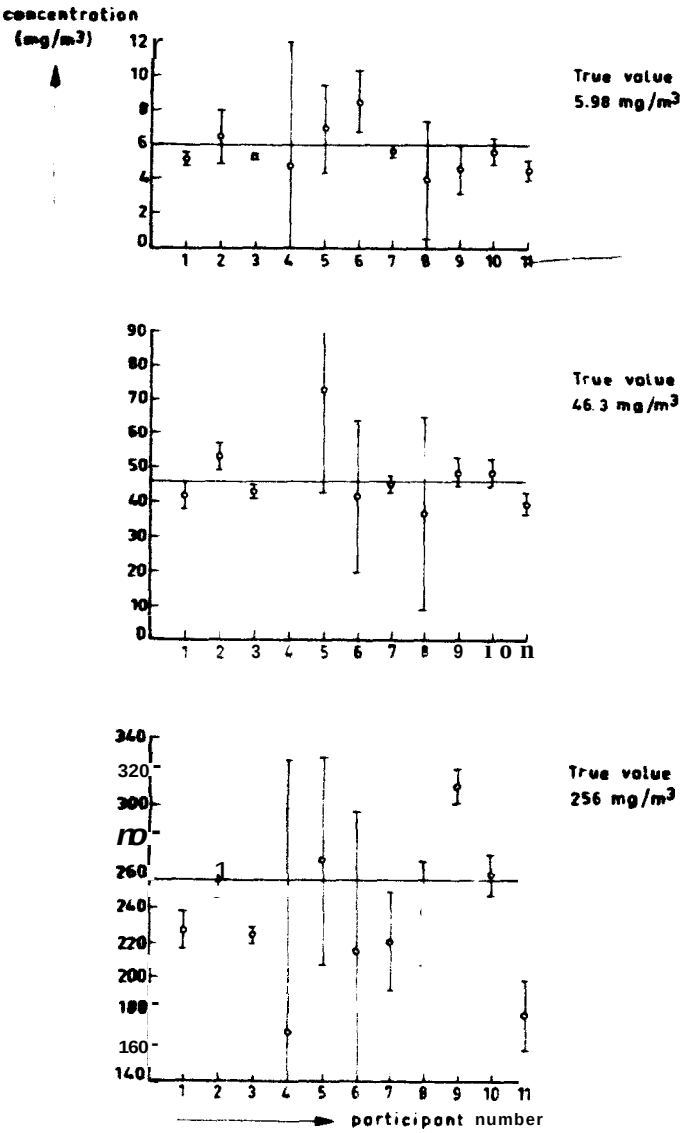


Figure 4—Round-rabin test for chlorinated hydrocarbons Results of analysis of trichloromethane Mean values and 95% confidence intervals.

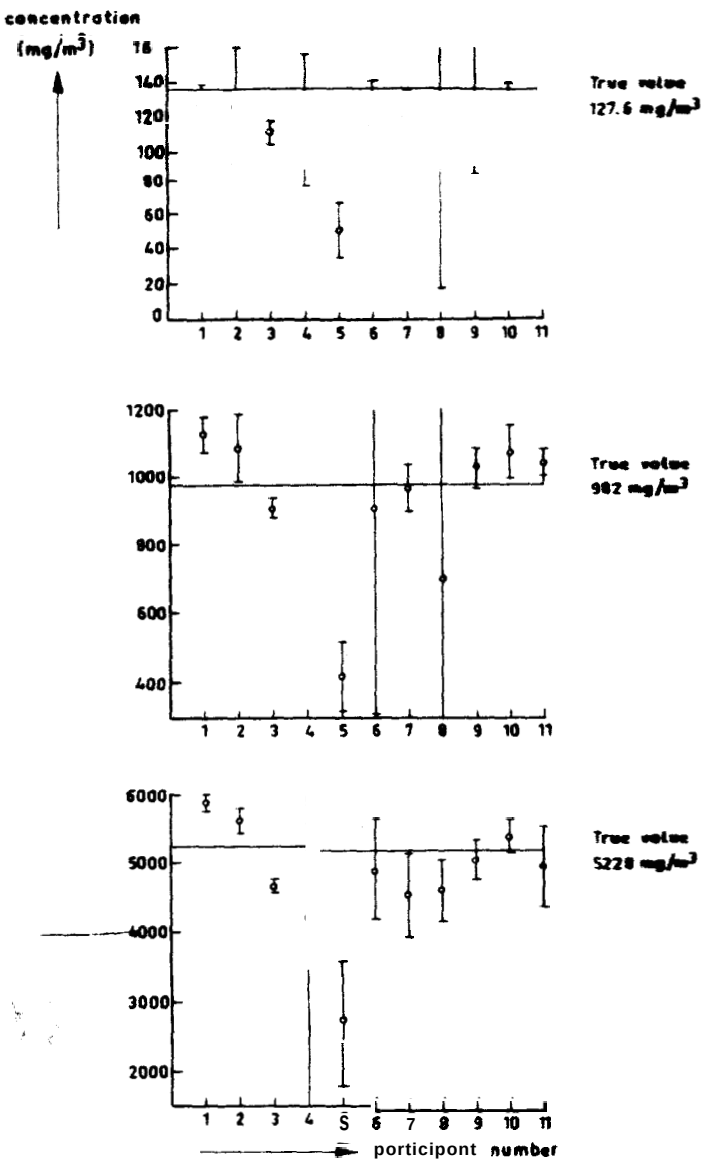


Figure 5—Round-robin test *for* chlorinated hydrocarbons. Results of analysis *of* trichloroethane. Mean values and 95% confidence intervals.

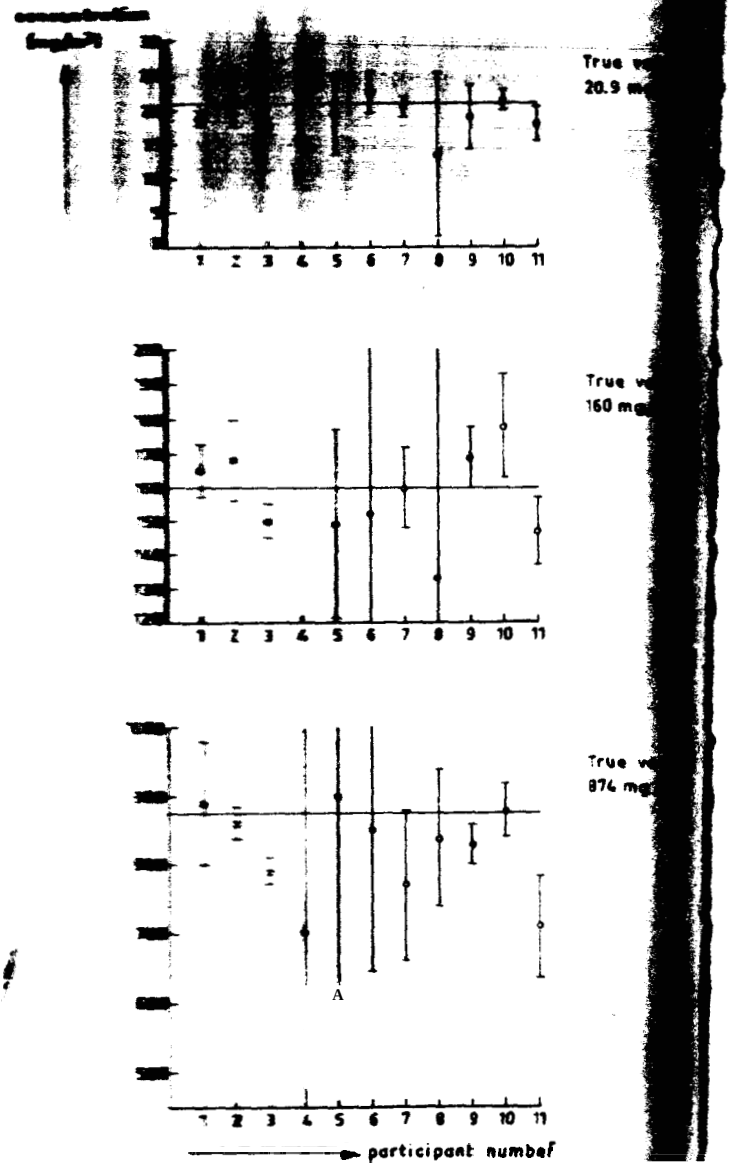


Figure 6—Round-robin test for chlorinated hydrocarbo
Results of analysis of trichloroethene. Mean values and 9
confidence intervals.

conditions (same operator. same apparatus. same laboratory, and a short interval of time). may be expected to lie with a specified probability In the absence of other indications, the probability is 95%. The reproducibility R is the value below which the absolute difference between two single test results obtained with the same method on identical test material, under different conditions (different operators, different apparatus, different laboratories and: or different time), may be expected to lie with a specified probability; in the absence of other indications, the probability is 95%. Cochran's test and Dixon's test are explained in Reference 3.

Briefly summarized, the procedure of the statistical evaluation is as follows:

1. The results are inspected for peculiarities such as systematically high or low values within one laboratory missing values, etc.
2. The variances per "cell"(= group of results per labora-

tory and per cell are calculated in the normal way.
3. The variances per cell are then compared with e
other by means of Cochran's test. In this test, the gre
est variance s divided by the sum of all variances:

$$C = \frac{s^2_{max}}{\sum_{i=1}^{P} S_i^2}$$

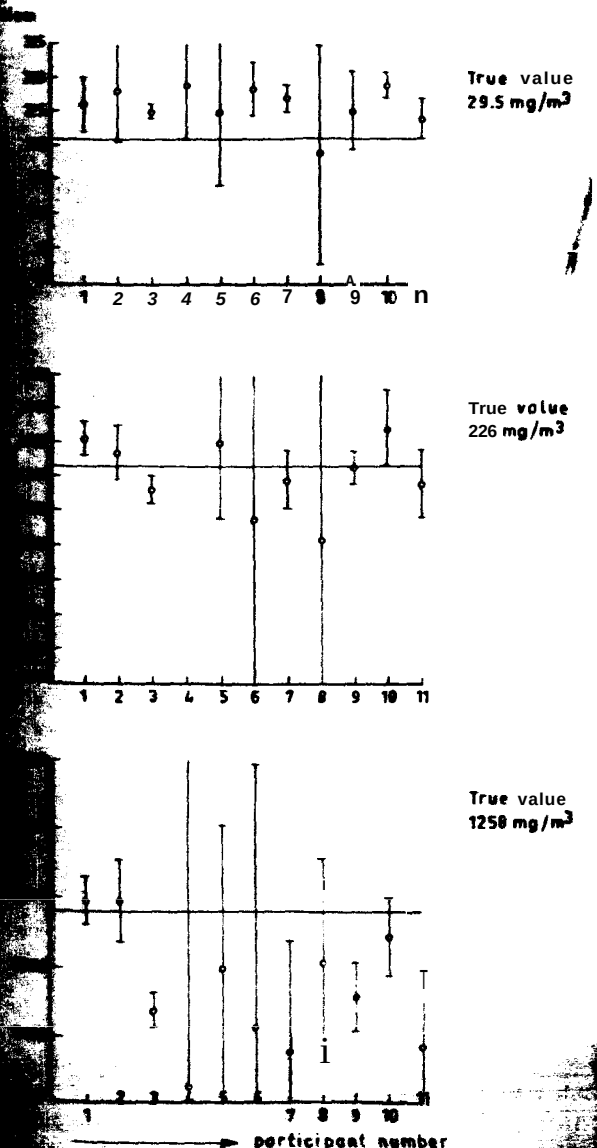
The result is tested against a table of critical va
on the number of laboratories and
of replicates per concentration.[3] If th
the 1% level in the table, the result wit
greatest variance is considered as an outlier. If the
exceeds the 5% level, the result is considered
straggler. Outliers are eliminated. Straggling value
examined by the statistical expert. If one labor
produces an exceptionally high number of straggl
can be
a outlying laboratory. If an o

...he test must be repeated with the remaining ... no more outliers are found

...ing values are subjected to Dixon's test. For ...e the mean values of the remaining cells are ... and ranked in increasing order, the result ..., Z_2, ... Z_H. Dixon's criterion depends on the ... of H (H being the remaining number of cells ...rmance of Cochran's test). In our case, Dix... is calculated according to the formulas:

$$Q_{11} = \frac{Z(2) - Z(1)}{Z(H-1) - Z(1)} \text{ and } \frac{Z(H) - Z(H-1)}{Z(H) - Z(2)}$$

...g the test criterion, Z is the mean value of each ...tory per level and H the laboratory with the high... value. The greatest of the two values of Q_{11} is ... against a table of critical values[3] on 1% and on ...evel for outliers and stragglers.



...nd-robin test for chlorinated hydrocarbons ...lysis of tetrachloroethene. Mean values and ...ence intervals.

5. Finally, r and R are calculated from the remaining values.

The tests are fully explained in Reference 3.

Results

Cochran's test requires an equal number of replicates per concentration for each participant. A number of concentration cells did not comply with this requirement. In order to make these cells suitable for inclusion in the calculation of repeatability and reproducibility, a number of values were eliminated from the complete concentration cells randomly. After this elimination, the Cochran and Dixon tests were computed again. This operation was performed with one, two and three eliminations per concentration cell. Incomplete concentration cells which had not been rejected at these stages were used for the calculation of repeatability and reproducibility.

The results of the statistical evaluation are presented in Tabk VI (the full statistical evaluation is available on request). In Table VII an overall picture of the outliers is presented. The tables show that 27% of the results are eliminated by Cochran's test. Eliminations are concentrated in Laboratories 5, 6 and 8. Furthermore, two results are rejected by Dixon's test. Further investigation has shown that these eliminations most likely are caused by an error in the preparation of the standards.

The general means of the results on carbon tetrachloride show deviations up to 80%. For the other compounds, deviations from the general mean vary from -9 to +5%, indicating that no bias is introduced by the method of sampling and analysis.

Comments of the Participants on the Proposal

Comments made by the participants of the round-robin test are:

- the method is not sensitive enough for determination of tetrachloromethane in the concentration range of interest;
- for analysis of mixtures of solvents, capillary columns are more suitable than packed ones. It is suggested that a list of suitable columns be included in the Standard;
- the proposal concerns compounds with entirely different applications. A more distinct description of compounds which can be determined simultaneously is necessary.
- inclusion in the Standard of a simple method for purification of CS_2 in case the concentrations of contaminants are unacceptably high is suggested;
- one of the participants states that a more systematic study of the contribution of the different sources of errors should be performed. If the inaccuracy of the volume determination appears to be a major error source, alternative sampling methods should be considered;
- the choice of chemical substances are not in accordance with IUPAC nomenclature.

The fact that about 10% of the charcoal tubes were not loaded

TABLE IV
Desorption Efficiencies

Participant number	Desorption efficiency					
	CCl_4	$CHCl_3$	CH_3CCl_3	$CHClCCl_2$	CCl_2CCl_2	not specified per compound
1						[illegible]
2						•
3	88	93	94	93	92	
4	100	99	98	99	97	
5						[illegible]
6						96
7	96	102	95	100	99	
8	100	100	100	100	99	
9						100
10						95
11	98	97	99	99	96	

[illegible] not specified

with any test material is remarkable. The origin of this phenomenon is not clear.

Most common sampling failures can be discounted in this experiment:

- ***Leakage between charcoal tube and pump.*** This possibility is excluded by the fact that the sampling flow was determined with the charcoal tube in line.
- ***Pumpfarlure.*** Working of the pump could be ascertained by the fact that some pumps had a stroke counter and on others running of the pump was clearly visible by movement of the belt.
- Low ***adsorption efficiency.*** No breakthrough was observed.
- ***Losses during transit or storage.*** In this case an equal loss of analyte from all tubes would be expected.
- ***Failure of the sampling system.*** This possibility can virtually be excluded. Any small leakage of the sampling system will cause a considerable lowering of the concentration of the material downstream of the leakage due to a venturi effect. This was found neither in the samples nor on the monitor. Furthermore, it is very unlikely that all sampling air will be extracted from the leakage.
- ***Poor loading of the*** tubes. Although the three participants who were confronted with unloaded sample tubes used the same make and lot of charcoal tubes, six other participants using the same tubes did not suffer from this phenomenon. Consequently, the sampling failures certainly cannot be assigned to the charcoal tubes as such. The strong differences in adsorption efficiencies of chlorinated hydrocarbons found in another experiment in which the test atmosphere was generated in an independent way, however,[6] lead to the conclusion that sampling of chlorinated hydrocarbons is less straight forward than it seems to be.

From Table VII it can be concluded that the number of outliers differs strongly per participant. Four laboratories are responsible for 85% of the outliers. From the reply form three major causes of error can be assigned:

1) In a few cases the results of one component deviate throughout the test. This can be assigned to failures in the preparation of the standards.

2) In some cases the amount of material found on the tu was in reasonable agreement with that on the other tu but the volume of air sampled differed strongly fro other volumes. A failure in volume determination, due to lack of constancy of the pump, may be the cau the failure.

3) In most cases concentrations of all five components w too low on one tube. Poor loading of the sample tube m be the cause of the failure in these cases; however, n single laboratory reported a breakthrough.

Apart from these possible failure causes, a critical co parison of the work-up and analysis procedure of the dif ent laboratories is necessary to eliminate possible ambi ties in the proposal.

Concerning the quality of the method, the follow guidelines for the reproducibility are

up to 25%: good
25-50%: acceptable
more than 50%: unacceptable

Comparison of these criteria with the results in Table suggests that the method is not suitable for the determi tion of tetrachloromethane and trichloromethane. Impro ments are necessary. For the other three compounds, reproducibility is sufficient for practical use. For tric

TABLE V
Breakthrough of Chlorinated Hydrocarbons on Charco Tubes Containing 150 or 1000 mg of Coconut Charco Given as Percentage in Back-up Section

Charcoal tube	150 mg	1000 mg			
Volume sampled (dm^3)	6	7	19	25	3
Analyte[A]					
trichloromethane	56.0	<0.1	<0.1	13.0	5
tetrachloromethane	34.0	<0.1	<0.1	*3.0*	1
1,1,1-trichloroethane	59.0	<0.1	<0.1	5.0	2
trichloroethene	< 0.1	<0.1	<0.1	< 0.1	<
tetrachloroethene	< 0.1	<0.1	<0.1	< 0.1	<

[A] A mixture of analytes is applied at the highest concentration l of the round-robin test.

TABLE VI
Round-Robin Test for Chlorinated Hydrocarbons in Air
Summary of All Results

Compound	Level	Uns	Coc	Dix	True value	General mean	Bias %	Repeatability absol	Repeatability rel %	Reproducibility absol	Reproducibility rel %
CS_2	1	2	3	0	1.57	1.74	+10	0.92	53	2.05	118
CCl_4	2	1	4	0	12.0	21.6	+80	3.1	14	37.1	171
CCl_4	3	0	3	0	85.7	120.4	+40	13.8	11	161.5	134
$CHCl_3$	1	1	2	0	5.98	5.76	-4	1.58	27	3.89	68
$CHCl_3$	2	1	3	0	46.3	45.5	-2	4.7	10	13.5	30
$CHCl_3$	3	0	5	0	256.0	241.9	-5	17.4	7	126.1	52
CH_3CCl_3	1	1	3	1	128.0	127.0	0	12.6	10	23.7	18
CH_3CCl_3	2	1	2	1	982.0	1034.0	+5	88	8	231.0	22
CH_3CCl_3	3	0	2	0	5238.0	5088.0	-3	640.0	12	1384.0	27
$CHClCCl_2$	1	1	2	0	20.9	20.1	-4	4.0	20	6.2	30
$CHClCCl_2$	2	1	3	0	160.0	162.0	+1	15.0	9	34.0	21
$CHClCCl_2$	3	0	3	0	874.0	821.0	-6	103.0	12	202.0	24
CCl_2CCl_2	1	1	3	0	29.5	26.6	-9	5.3	20	7.4	28
CCl_2CCl_2	2	1	3	0	226.0	228.0	+1	22.0	9	44.0	19
CCl_2CCl_2	3	0	3	0	1258.0	1183.0	-6	138.0	11	273.0	23

Explanation: Uns = less than 5 replicates per cell; Coc. = Cochran elimination (poor repeatability); Dix = Dixon elimination (poor reproducibility); Concentrations are given in mg/m^3.

...he CS_2 which is used as the desorbing liquid acts ...ence under certain analysis conditions. The ... of tetrachloromethane may suffer from inter- ...zene which is present as an impurity in some ...e. In both cases, a considerable improvement ...ted from prescription of an electron capture ...he determination of compounds which have a ...tivity as well as low MAC value, as for CCl_4 ... this case.

...hat about 10% of the charcoal tubes were not ...h any test material needs further elucidation. ...tion exists between this phenomenon and ... number of the charcoal tubes.

...od is not suitable for the determination of ...oromethane and trichloromethane. Improvements ...ry.

...loroethene, 1,1,1-trichloroethane and trichlo- ...e repeatability of the determination ranges ... 10% to 20% and the reproducibility from ... to 30% (cf Table 6). This is sufficient for ...e.

...on of results is due to failures in preparation of ...ards, failures in volume determination and poor ...on. The latter is regarded as the major cause of ...

...improvement of the method is prescription of ...n capture detector instead of a flame ionization ... for compounds with a low FID sensitivity and ...C values.

Acknowledgments

This study has been performed on behalf of the Dutch General Direction of Labour (Ministry of Social Affairs and Employment) which has supported this study financially. The dedicated technical assistance of Mr. A.M.M. Moons and Mr. H.L.M. Verhagen as well as the helpful discussions with Drs. J.C.T. Hollander, Ir. F.L. Schulting and Ir. J. Stellingwerf are gratefully acknowledged.

ISO documents may be obtained from the National Standards Institutes. For the U.S.A.: American National

TABLE VII
Summary of Outlying Concentration Cells

Compound	CCl_4	$CHCl_3$	CH_3CCl_3	$CHCl\ CCl_2$	CCl_2Cl_2
	Outliers[A]				
Level	1 2 3	1 2 3	1 2 3	1 2 3	1 2 3
Participant no.					
1	C				
2	CC		C		C
3					
4	UUC	UUC	UUC	UUC	UUC
5	CC	CCC	DDC	CCC	CCC
6	CCC	CC	C	CC	CC
7		C			
8	C	CCC	CC	CC	CC
9	U		C		
10					
11					
Total number of eliminations	5 5 3	3 4 5	5 4 2		4 4 3

[A]U = less than 5 replicates per cell
C = Cochran outlier
D = Dixon outlier

Standard[illegible] 1430 Broadway, New York, NY 10018. For [illegible] of the Institutes are obtainable from [illegible] Standards Organisation, 1, Rue de Var[illegible]ve 56, CH 1211 Genève 20, Switzerland: Tele[illegible] CH.

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5 November 1984: Revised 19 June 1985