



NEW APPLICATIONS OF OIL DISSOLVED GAS ANALYSES AND RELATED PROBLEMS

Paper presented in the name of Study Committee 15

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Summary

Dissolved-gas-in oil chromatographic analysis is successfully applied to fault detection in the maintenance of large power transformers. Savings achieved are in the 100 Million \$ range.

With increasing sensitivity Gaschromatography can be applied to the surveillance of design and type tests. Slight gas evolution during such a test is an indication of a deterioration of the electrical insulation, which may be effective only after years. Precision and accuracy of gaschromatographical measurement determine repeatability and reproducibility of such measurements. They give an indication of the smallest difference in gas contents being measurable significantly. The state of the technique must be improved to improve repeatability and reproducibility.

Keywords

Gaschromatography - dissolved gases - repeatability - reproducibility - Statistics.

1. Introduction

Dissolved-gas-in-oil chromatographic analysis (abbreviated: oil dissolved gas analysis) was begun to be studied in the 1960ies in two parallel ways:

- investigation of gases being developed in power transformers and measuring transformers in service and comparison with discovered defects in these apparatus,
- investigation of the deterioration of hydrocarbons by thermal and electrical influences, being based on kinetics of chemical reactions.

As a result oil dissolved gas analysis was applied to monitoring oil filled high voltage power apparatus in service with gas contents above 100ppm (parts per million). In the late 1970ies gaschromatography was begun to be applied to check high voltage power apparatus on defects during type or design tests in the single ppm-range.

1.1 Monitoring oil filled high voltage power apparatus in service by oil dissolved gas analysis.

For the diagnosis of defects in power transformers,

reactors, instrument transformers, capacitors and bushings several guides were developed [1-6]. They give defined ranges for ratios of gas contents (hydrogen, methane etc.) linked with specified defects, namely overheating and electrical discharges. Limiting values for the safety in operation are determined by the Electricity Generation Boards. Sampling and gaschromatographic methods and diagnostic guides were coordinated by CIGRE Task Force 01 of WG 15-01 (Fluid impregnated systems) and by IEC Working Group 10A/02 resulting in the IEC Publications 567/1977 [7] and 599/1978 [1]. By applying oil dissolved gas analysis to the detection of incipient faults amounts in the 100 million \$ range in outage/reduced costs could be saved up to now.

1.2 Oil dissolved gas analysis as a means for checking electrical type and design tests.

With the successful application of oil dissolved gas analysis above the 100ppm range to the diagnosis of oil impregnated high voltage power apparatus and with steadily increasing sensitivity and precision of gaschromatography new applications could be envisaged such as the measurement of small differences (single ppm) of gas contents. Thus type and design test results of these high voltage power apparatus may be checked with respect to slight gas evolution.

Very sensitive surveillance of type and design tests becomes more and more important. For the reduction of costs of high voltage power apparatus in severe competition stresses and exploitation of material have to be increased to reduce dimensions and material. To warrant safety of operation in service, design, routine and type tests must be correlated to the longterm behaviour under operating conditions in a way, that rather slow chemical and electrochemical reactions are anticipated. Accordingly these test results must be checked themselves; to detect if even only slight deficiencies have been initiated. These deficiencies are an indication of the longterm effect of service conditions - anticipated and concentrated by a type or design test - which could in time deteriorate the insulation and interrupt by breakdown as spectacular consequence the operation of high voltage networks; as experienced in Europe and the United States.

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Such tests are heat run tests of power transformers [8], 600 chopped waves for instrument transformers [9] or long time partial discharge tests at elevated stresses. Oil dissolved gas analysis can be a method for the surveillance of such tests, if the precision of measurement is high enough to guarantee the significance of very small differences in gas contents in the single ppm range, indicating a small but eventually dangerous deterioration of the insulation. If these measurements are used by purchasing authorities as basis for acceptance tests of a series of apparatus, it is important and urgent, to know the extent to which successive measurements in a given laboratory or measurements in different laboratories using the same specimen, give consistent results [10]. (The sensitivity limit given in IEC Publication 567/1977 [7] clause 7.1 are not sufficient for these demands, whereas the low repeatability of 5% as given by IEC 567/1977 [7] cannot be followed in the single ppm-range.)

Therefore at the meeting of Study Committee 15 in Prague September 1983 it was decided that the Task Force 01 of WG 15-01 (Fluid impregnated insulating systems) must investigate the significance of differences in measurements of gas quantities (single ppm-range) dissolved in insulating oils of high voltage power apparatus, by gaschromatography.

Work was started immediately and Round Robin Tests were performed November 1983, January and May/June 1984.

They showed in which steps of the procedure - from taking the oil dissolved gas samples through to the measuring results - the conditions were found to be about satisfactory. But wider spreads of results than expected made clear which steps have to be investigated in detail for improvements of accuracy and of significance in differences.

In view of the increasing commercial importance of such tests which are being used as acceptance criteria, these results and related problems are reported.

2. Methodical procedure applied by the Task Force.

The central problem in applying gaschromatography to the evolution of small gas quantities in the single ppm range is the significance of the difference between two measured values, namely if the difference between the two measured values is a "true" difference. Because of inherent inaccuracies every quantity being measured several times, results in a statistical distribution of measured values around the "true" value. (Fig. 1 case A). All these measured values lie in an area of 6 standard deviations symmetrical around the "true" value. This means, that in an extreme case two measured values of one and the same "true" value lie 6 standard deviations apart (Fig. 1 case A, A1 and A2). For a "true" value of 10 ppm Hydrogen e.g. with a standard deviation of 1 ppm, A1 could be =7 and A2=13. But if there are two "true" values (Fig. 1 case B) of B=10 and C=16, an extreme possibility could be, that B1=13 and C1=13 too, so that the measured values are equal, although the two "true" values are 6 standard deviations apart (same normal distribution presumed). No difference were found despite an increase of 60% of gas content from 10 to 16 ppm. As soon as the difference between the two true values is 7, at least a difference of 1 between measured values could be found and the difference is significant then. But on the other hand as long as the difference of measured values is smaller than 6 as in case A fig. 1, the "true" value could be the same. The standard deviation of the distribution of gaschromatographic meas-

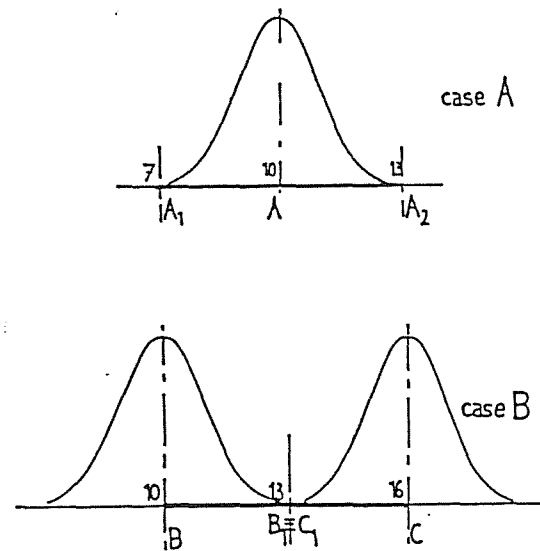


Figure 1 Distribution of measuring values. "True" value and measured value. Explanation see 2.

urements must therefore be kept as small as possible, which can only be achieved, if the factors influencing this spread are known and under control.

For the judgement about an eventual electrical deterioration furtheron the distribution of evolved gases in bushings, measuring transformers etc. with time and the ratio of oil volume to electrical active parts must be considered.

This report is based on the statistics given in ISO 5725-1981 [11].

2.1 Terms applied

- Repeatability r (ISO 5725-1981):

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 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%.

- Reproducibility R (ISO 5725-1981):

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%.

In the above and elsewhere in this International Standard, a single test result is the value obtained by applying the standard test method fully once to a single specimen, and as such may be the mean of two or more observations or the result of a calculation from a set of observations, as specified by the method.

Both values will be calculated from the test results according to ISO 5725-1981.

- Accuracy (ISO 3534-1977)[13]

2.83 accuracy of the mean: The closeness of agreement between the true value and the mean result

which would be obtained by applying the experimental procedure in very large number of times.

The smaller the systematic part of the experimental errors which affect the results, the more accurate is the procedure.

- Precision (ISO 3534-1977)[13]

2.84 precision: The closeness of agreement between the results obtained by applying the experimental procedure several times under prescribed conditions.

The smaller the random part of the experimental errors which affect the results, the more precise is the procedure.

It must be kept in mind, that despite excellent precision or/and repeatability the accuracy of a series of measurements by applying the same experimental procedure under prescribed conditions to the sample, may be poor. Whereas precision and repeatability are only a measure for the possible differences between measured values, accuracy is a measure for the possible difference of measured values to the "true" value. Repeatability is defined as the value, below which the absolute difference between two single measuring results is expected to lie, with a specified probability (in general 95%). But for the calculation of r , it is more accurate to have a higher number of measuring results than two, so it can be calculated from the standard deviation of all measuring results, and not just from two, which are always more random than e.g. five.

For the calculation of repeatability r and reproducibility R with a probability level of 95% the following two formulas are used:

$$\text{Repeatability } r = 2,83 s_r$$

$$\text{Reproducibility } R = 2,83 s_R$$

- s_r ... Repeatability standard deviation, calculated from the arithmetic mean of the variances of the p laboratories
- s_R ... Reproducibility standard deviation, calculated from S_r and the standard deviation of the mean values of all laboratories from the common arithmetic mean of all measured values.

The calculation for the two standard deviations are different for the three cases of numbers of measurements n per sample in the p laboratories (for formulas see ISO 5725-1981):

- 1) only two measurements $n = 2$
- 2) an equal number of measurements $n \geq 2$
- 3) different numbers n_1, n_2, n_3, \dots of measurements in the p laboratories.

- Outliers and stragglers (ISO 5725-1981):

Entries among the original test results, or derived from them, that deviate so much from comparable entries, that they are considered as irreconcilable with the other data. Outliers are with 99%, stragglers with 95% irreconcilable.

Outliers and stragglers are determined by the Cochran's maximum variance test [11]. If the number of measurements is e.g. $n = 6$, and the number of laboratories $p = 5$, then the biggest variance of all laboratories must be greater than 0,506 respectively 0,588 times the sum of all variances, to be a straggler, resp. an outlier.

Outliers and stragglers are excluded from data evaluation. This Cochran's test does only apply to standard deviations; for a mean value of a laborato-

ry the difference to the common mean of all laboratories must be much higher, the outlier/straggler must differ at least 4 standard deviations s_R from the common mean. The experimentally determined repeatability r - after exclusion of outliers and eventually of stragglers - is a measure for the difference between two measured values of one and the same "true" value. As long as the difference between two measured values, e.g. before and after a type test, is smaller or equal to the repeatability, it can not be considered as a significant difference. Only a difference between two measured values being greater than the repeatability can be accepted as significant, presuming, that these two measured values were obtained with the same method under the same conditions (same operator, same apparatus, same laboratory) and a short interval of time to having taken the samples. Reproducibility R is better not taken as a measure for gas evolution during type or design tests, these comparisons should always be performed by the same laboratory, on behalf of the fact, that reproducibility is generally worse than repeatability. And the aim must be, to achieve a significant difference, which is as small as possible, so already slight gas evolutions can be detected with high probability.

2.2 Factors influencing the accuracy of dissolved gas-in-oil chromatographic analysis.

To be able to detect already slight gas evolution with high probability, the main factors which increase the spread of measured values for one and the same "true" value must be identified. The main factors are:

- Gaschromatographic procedure including calibration and minimum detectable limits,
- Relative gas content in the oil sample,
- Sampling point,
- Sampling vessel,
- Sampling method,
- Sample storage and transport,
- Time interval between sampling and analysis,
- Gas extraction from the sample,
- Transfer of the extracted gas to the Chromatograph.

2.2.1 The Gaschromatograph.

The basic influence on accuracy, precision, repeatability and reproducibility of oil dissolved gas analysis lies in the Gaschromatograph itself. To investigate this influence for itself the Gaschromatographs of the participating laboratories have to be tested with one and the same calibrating gas mixture. Therefore in the first Round Robin test two bottles of extra high accuracy calibrating gas were transported by car directly from one laboratory to the next one within ten days. In parallel, this extra high accuracy calibrating gas was filled into evacuated glass bulbs and transported to several laboratories to check the influence of sampling and transport.

Obviously for gas dissolved in oil samples the repeatability must be worse because of all the additional influences. The repeatability depends primarily on the minimum detectable limits. How these minimum detectable limits for gases dissolved in oil have improved, shows Table 1:

Gas	IEC 567[6]	CIGRE 12-01/1982[11]	Electra 82[8]
H ₂	5	2	2
CO ₂	25	5	10
CO	25	5	5
CH ₄	1	0,3	0,1
C ₂ H _n	1	0,3	0,1

Table 1 Minimum detectable limits for microliters of gas dissolved in one liter of oil (ppm).

In these limits the influences of all the other factors mentioned above are included.

The minimum detectable quantity or sensitivity as a measure of significance is mentioned in IEC Publication 599/1978[1]: Before considering, that any gas is present in significant quantity, its concentration should be at least ten times these sensitivity limits. The final report of working group 06 of Study Committee 12 (Transformers) in Electra 82[8] tolerates as gas evolution during 12 hours heat run tests 10% of the original gas content plus 2 times the minimum detectable quantity as a general formula, respectively plus 5 to 11 times in fact for the specified gases. [9] however tolerates fixed values, which would for a gas content of 10ppm before the test correspond also to 10% of this original gas content, but plus c.2 to 10 times the minimum detectable quantity. To this pragmatismal respectively hypothetical stipulation of significant differences from ISO 5725-1981[11] or vice versa is no direct mathematical derivation. Both points of view - the statistical and that of the minimum detectable quantity - will be applied to the results of the three Round Robin tests and compared to each other.

The calibration of the Gaschromatographs was performed either by pure gases or by calibrating gas mixtures.

All analytical procedures (type of columns, number of injections, temperature program, detectors, special additional parts) were registered for comparison purposes.

The influence of the relative gas content in the ranges of 10, 100 and 1000 ppm was investigated in the second and third Round Robin Test.

2.2.2 Sampling: Origin, point, vessel, method, storage, transport, interval to analysis.

All information about sampling concerning the pure gas analysis in the first Round Robin test is given in 2.2.1 first paragraph.

Gas-dissolved-in-oil samples:

- Origin of samples. In the first and second Round Robin test (RR) all oil samples to the various laboratories had common origin, namely from a rubber bellows with a prepared oil gas mixture for the first RR and from two large power transformers in service for the second one. In the third RR for the investigation of the repeatability the laboratories prepared samples individually, either from power transformers or from individually prepared oil-gas-mixtures.
- Point of sampling. In the first RR all samples were taken directly from the rubber bellows, in the 2. and 3. RR from the sampling valves of the power transformers or from the artificial mixture vessel directly.
- Sampling vessels and method. Depending on the destination, for all three RR either glass syringes

(20, 50 or 100 ml), gas tight syringes, glass tubes, glass bottles or metallic bottles were used. They were filled in conformance with IEC 567/1977 either under vacuum or after thoroughly rinsing by an instructed person.

- Storage and transport of samples. All sampling vessels were protected against light, in as far as necessary. In the 1. RR the main part of sampling vessels was transported by one person in the same car (together with the high accuracy calibrating gas bottles), a few by mail for comparison purposes. In the 2. RR the sampling vessels were transported partly by the person having taken the samples, partly by transportation firms or by mail.
- Interval to analysis. In general all analysis were performed within one fortnight after sampling. In the 1. RR a check analysis was performed on a sample having undergone the whole round tour.

2.2.3 Gas extraction from the sample and transfer to the Gaschromatograph.

In principle three methods were used: according to IEC 567/1977[7]

- Toepler pump method, transfer of the gas either by syringe or directly into the sample loop.
- Stripping method by injecting via syringe a defined quantity of the gas-dissolved-in-oil sample into the bubbler.
- Partial degassing method, transfer of the gas either by syringe or directly into the sample loop.

3. Results of the three Round Robin Tests

3.1 General

The about 1800 measuring values of the three Round Robin Tests are summarized in the following tables. They contain:

- the minimum detectable quantities S_d (sensitivities) of the analyzed gases,
- the number p of participating laboratories,
- the number of outliers and stragglers excluded from calculation,
- the range of the averages \bar{y} (arithmetic means) and standard deviations s, or differences w of two samples, of the laboratories included in the calculation,
- the common average m of the included laboratories,
- repeatability r and reproducibility R according to ISO 5725-1981 in ppm and in % of m,
- the relation to the minimum detectable quantities S_d (sensitivities) from Table 1 according to the formulas:

$$r = 0,1 m + z.S_d$$

$$R = 0,1 m + Z.S_d$$

All calculations are performed according to ISO 5725-1981, clause 14.

Outliers and stragglers were determined according to clause 14 or a deviation of a laboratory's mean of $\geq 4 S_R$ from the common mean.

3.2 Comparative measurements of high accuracy calibrating gases in the first RR.

Results in Table 2 are calculated according to formulas in clause 14.9 Uniform level experiment with $n \geq 2$ replicates per cell (laboratory) of ISO 5725-1981 with a number n of analysis per laboratory between 1 and 14.

	Dimension	H2	CH4	C2H4	C2H6	CO	CO2
Sd	ppm	2	0,1	0,1	0,1	5	5
Calibrating gas	ppm	11,5	9,6	10,3	10,6	18,0	19,3
Outliers excluded	-	3	1	-	-	-	2
remaining p labors	-	6	10	11	11	8	6
\bar{y} Min.	ppm	11,2	9,1	8,3	9,5	12,1	15,0
\bar{y} Max.	ppm	15,5	10,3	11,6	13,0	21,2	21,6
s Min.	ppm	0	0,1	0,01	0,1	0,7	0,4
s Max.	ppm	0,4	1,1	0,6	0,8	1,8	1,1
average m	ppm	12,3	9,6	9,6	10,3	17,3	18,6
r	ppm	0,9	1,4	0,9	1,1	3,7	2,4
	% m	7,3	14,6	9	11	21	13,6
z in	-	-	-	-	-	-	-
$r=0,1m+z.Sd$	-	$r<Sd$	4,4	-	1	0,4	$r<Sd$
R	ppm	4,0	1,5	2,8	2,3	9,6	4,7
	% m	32	15,6	29	22	55	24,7
Z in	-	-	-	-	-	-	-
$R=0,1m+Z.Sd$	-	1,4	5,4	19	13	1,6	$R<Sd$
Outliers included p	-	9	11				8
average m	ppm	15,7	9,9				22,9
r	ppm	7,0	1,4				8,3
	% m	45	14,1				36
z in	-	-	-	-	-	-	-
$r=0,1m+z.Sd$	-	3,2	4				1,2
R	ppm	20,6	6,9				26,9
	% m	131	70				117
Z in	-	-	-	-	-	-	-
$R=0,1m+Z.Sd$	-	9,5	60				5

Table 2. Comparative measurements of high accuracy calibrating gases by 11 laboratories. Explanations see clause 3.1. The values of the calibrating gas are reference values, not "true" values: r and R are calculated from corresponding averages m.

Table 2 shows, that the analysed gases were measured within a repeatability of 20%, if outliers are excluded. The glass bulbs with teflon cocks filled with the high accuracy calibrating gases and sent to three laboratories gave no satisfying results: the deviation was in all cases above 20% from the guaranteed value mostly even above 100%!

The Round Robin Test with high accuracy calibrating gases, directly taken from the metallic (original) bottles, can be considered as satisfactory concerning repeatability and reproducibility with respect to the low ppm-content of about 10 ppm.

3.3 Comparative measurements of oil-dissolved-gas samples.

The results of the first Round Robin test are given in Table 3, those of the second RR in Table 4 and 5 for the oil samples from transformer 1-2 and 3-4 respectively. Whereas in the first RR repeatability is in half cases above 60% and reproducibility even above 100%, in the second RR more than half the cases are below 10% for r and below 75% for R. The $r=300\%$ for Hydrogene must be considered as an outlier. One reason for these great difference may be caused by the sampling vessels: in the 2. and 3. RR each laboratory used its own habitual sampling vessels. A second not unimportant reason may be, that after the disappointment of the first RR special attention was paid to every detail, avoiding "routine work" of 1000ppm-analysis. On the other hand the homogeneity

of the samples of the 1. RR could be questioned. Concerning reproducibility must be mentioned, that the applied methods were not exactly the same in every detail for all laboratories. The applied 95% probability level is a matter of agreement, which can be discussed.

	Dimension	H2	CH4	C2H4	C2H6	CO	CO2
Sd	ppm	2	0,1	0,1	0,1	5	5
Stripping method							
Outliers excluded	-	-	1	-	-	-	-
remaining p labors	-	4	3	4	4	4	4
\bar{y} Min.	ppm	5,7	17	11	5,5	29	47
\bar{y} Max.	ppm	9,5	21	13,8	13,5	50	160
w Min.	ppm	0	0	0	1	2	5
w Max.	ppm	3,4	1,1	1,6	7,6	56	83
average m	ppm	6,8	20	12,3	10,8	39,6	105
r	ppm	4,2	1,3	1,9	9,2	64	103
	% m	62	64	15,4	86	162	98
z in	-	-	-	-	-	-	-
$r=0,1m+z.Sd$	-	2	$r<10\%$	7	81	12	18
R	ppm	6	7,5	3,9	12	64	157
	% m	90	38	31,5	112	162	150
Z in	-	-	-	-	-	-	-
$R=0,1m+Z.Sd$	-	3	33	27	100	12	29
Toepler resp. partial degassing method							
Outliers excluded	-	1	1	1	-	-	1
remaining p labors	-	7	7	7	8	6	6
\bar{y} Min.	ppm	1,5	5,3	1,4	0,2	5,5	13
\bar{y} Max.	ppm	15,2	17,8	10,2	14,2	55,2	133
w Min.	ppm	0,3	0,3	0,2	0,1	0,5	3,2
w Max.	ppm	2,9	3,3	2,8	2,4	16,2	30
average m	ppm	8,8	9,2	6,7	3,2	22,0	67
r	ppm	3,0	2,8	2,2	2,6	16,9	25,3
	% m	34,4	31	33	80	77	38
z in	-	-	-	-	-	-	-
$r=0,1m+z.Sd$	-	1	19	15	23	3	4
R	ppm	14,5	12,5	11,0	12,9	50,4	133
	% m	165	136	164	400	230	200
Z in	-	-	-	-	-	-	-
$R=0,1m+Z.Sd$	-	7	116	103	126	10	25

Table 3 Comparative measurements of 1. RR with gas extraction by Stripping or Toepler resp. partial degassing method. Explanations see clause 3.1. Number of samples analysed per laboratory n = 1 or 2, all taken from the same rubberbellows.

An influence of the calibration method, using calibration high accuracy gas mixtures or using single pure gases, could not be deduced from the measuring results.

Concerning sampling vessels, storage of samples and interval to analysis already known experience was confirmed. It must be emphasized, that

- gas tight syringes must be tested thoroughly especially with respect to H2-diffusion and air-inflow,
- cocks and valves are material dependant, e.g. Teflon is not applicable for long time transports,
- the protection of oil samples against light is essential. Gas contents are changed completely,

- especially in the single ppm range time between sampling and analysis should be kept below a fortnight,
- persons taking samples must be well trained, especially for oils with gas contents in the single ppm range.

Dimension	H2	CH4	C2H4	C2H6	CO	CO2
Sd ppm	2	0,1	0,1	0,1	5	5
Stripping method						
Outliers excluded	-	-	-	-	-	-
remaining p labors	3	4	4	4	3	4
\bar{y} Min. ppm	1	119	10	588	108	2160
\bar{y} Max. ppm	6	133	18	652	147	3740
w Min. ppm	0	2	0	5	0	10
w Max. ppm	8	7	0,3	26	3	60
average m ppm	3,7	125	12,6	612	96	2968
r ppm	11,3	10,3	0,4	38	4,3	86
z in % m	307	8,2	3,3	6	4,4	2,9
r=0,1m+z.Sd	5	-	-	-	-	11
R ppm	11,3	20,5	10,2	79	186	2077
Z in % m	307	16,4	81	13	194	70
R=0,1m+Z.Sd	5	80	90	180	35	410
Toepler resp. partial degassing method						
Outliers excluded	-	1	1	-	-	1
remaining p labors	7	7	8	8	7	7
\bar{y} Min. ppm	3	82	6	142	62	2050
\bar{y} Max. ppm	8	115	10,5	458	124	2860
w Min. ppm	0	0,5	0,1	12	2	27
w Max. ppm	0,8	11	1,6	91	11	293
average m ppm	6,3	93	8,1	354	100	2517
r ppm	0,7	6,9	1,8	109	11	336
z in % m	11	7,5	22	31	11	13
r=0,1m+z.Sd	r<Sd	-	10	740	-	17
R ppm	5,1	29,9	4,2	297	60	336
Z in % m	81	32	52	84	60	13
R=0,1m+Z.Sd	2	200	34	>1000	10	17

Table 4 Comparative measurements of 2. RR Trafo 1-2. Gas extraction by Stripping or Toepler resp. partial degassing method. Explanations see clause 3.1. Number of samples analysed per laboratory n = 1 or 2.

A very important fact common to both RR's is the trend in differences of averages m between the two gas extracting methods. Stripping shows lower means for H2, but higher ones for CH4, C2Hn and CO2 than the Toepler resp. partial degassing method. The differences of m in the two methods are being investigated by the Task Force. A first step was the 3. RR for analysing the repeatability in the participating labors by just measuring their own samples. So, long transports, influences of sampling, sampling vessels and long time intervals to analysis could be reduced. Table 6 gives a survey of repeatabilities found in the three RR's. The third RR shows:

- the Stripping method shows for CH4, C2H6 and CO lower repeatability values than the Toepler method. As only three laboratories were involved with Stripping, but eight with Toepler, these results will be checked in a further RR.
- stripping shows only small differences between the repeated analysis of the contents of one and the same syringe and the analysis of several syringes

with oil from the same object.

- the repeatability r in percentage of the average m seems to be improving with increasing ppm-values of gas content: with Toepler the 10ppm level has higher values than the 1000ppm level. For Stripping these values will be checked.

Dimension	H2	CH4	C2H4	C2H6	CO	CO2
Sd ppm	2	0,1	0,1	0,1	5	5
Stripping method						
Outliers excluded	-	-	-	-	-	-
remaining p labors	3	4	4	4	3	4
\bar{y} Min. ppm	1	125	9	534	106	1385
\bar{y} Max. ppm	5	160	10,5	621	165	2580
w Min. ppm	0	0,3	0,3	1,7	2	9
w Max. ppm	0	1,0	2,0	4,0	5	37
average m ppm	2,2	137	9,8	588	104	2025
r ppm	0	1,5	2,9	6,2	7,6	54
z in % m	0	1,1	29	1	7,3	3
r=0,1m+z.Sd	-	-	19	-	-	-
R ppm	6,2	45	2,9	109	88	1554
Z in % m	280	35	29	20	84	76
R=0,1m+Z.Sd	3	310	19	500	16	270
Toepler resp. partial degassing method						
Outliers excluded	-	1	1	1	1	1
remaining p labors	7	7	7	7	7	7
\bar{y} Min. ppm	3	85	5,7	252	32	1544
\bar{y} Max. ppm	7,4	110	11,0	451	115	2286
w Min. ppm	0	0,3	0,2	8	1	10
w Max. ppm	0,2	5,0	0,4	20	7	100
average m ppm	5,2	96	7,8	383	95	1803
r ppm	0,22	6,1	0,6	40	8,6	434
z in % m	4,2	6,4	7,3	11	9	24
r=0,1m+z.Sd	-	-	-	20	-	51
R ppm	4,57	16,2	5,1	932	85	668
Z in % m	88	17	65	255	90	37
R=0,1m+Z.Sd	2	66	43	>1000	15	97

Table 5 Comparative measurements of 2. RR Trafo 3-4. Gas extraction by Stripping or Toepler resp. partial degassing method. Explanations see clause 3.1. Number of samples analysed per laboratory n = 1 or 2.

- the values of repeatability for the Toepler method given in the 3. RR are higher than in the 2. RR and in the pure gas test of the 1. RR, which latter appears as consistent, as sampling and gas extraction have a strong influence.
- a repeatability r of 4 ppm for the 10ppm range and of 20 ppm for the 100 ppm range seems to be near realization for the Toepler method with the present state of the art. For the Stripping methods these values must be investigated.

4. Conclusions

As measurements of low gas contents in the single ppm range are very important for the surveillance of type and design tests of oil impregnated high voltage power apparatus, the values for repeatability and reproducibility have to be improved. The influences of the main factors on accuracy of gaschromatographic measurements from sampling through to in-

jecting the extracted gas into the gaschromatograph have to be further investigated.

Beside these measuring and preparing problems the distribution of evolved gases in bushings, measuring transformers etc. with time, and the ratio of oil volume to electrical active parts have an influence on the judgement about an eventual electrical deterioration.

			H2	CH4	C2H4	C2H6	CO	CO2
Sensitivity	Sd	ppm	2	0,1	0,1	0,1	5	5
High accuracy calibrating gases	m	ppm	12	10	10	10	18	19
	r	%	7	15	9	11	21	13
	R	%	32	16	29	22	55	25
1. <u>RR</u> <u>Stripping</u>	m	ppm	6,8	20	12,3	10,8	39,6	105
	r	%	62	64	15,4	86	162	98
	R	%	90	38	31,5	112	162	150
1. <u>RR</u> <u>Toepler</u>	m	ppm	8,8	9,2	6,7	3,2	22	67
	r	%	34,4	31	33	80	77	38
	R	%	165	136	164	400	230	200
<u>Stripping</u> TR 1-2	m	ppm	3,7	125	12,6	612	96	2970
	r	%	307	8	3,3	6	4,4	2,9
	R	%	307	16,4	81	13	194	70
TR 3-4	m	ppm	2,2	137	9,8	588	104	2025
	r	%	0	1,1	29	1	7,3	3
	R	%	280	35	29	20	84	76
2. <u>RR</u> <u>Toepler</u> TR 1-2	m	ppm	6,3	93	8,1	354	100	2517
	r	%	12	7,5	22	31	11	13
	R	%	81	32	52	84	60	13
TR 3-4	m	ppm	5,2	96	7,8	383	95	1803
	r	%	4,2	6,4	7,3	11	9	24
	R	%	88	17	65	255	90	37
<u>Stripping</u> laboratories	p	-	1	4	-	4	4	
	m	ppm	400	100	-	600	150	-
	r	%	-	8,2	-	5,2	4,9	-
each syringe two syringes	r	%	10	9,4	-	3,5	7,1	-
3. <u>RR</u> <u>Toepler</u> <u>Outliers</u> <u>labors</u>	-	-	0	to 2				
	p	-	3	to 9				
	r	%	31	25	-	24	35	
from sam- ples 100ppm	r	%	13	13	-	13	15	
	r	%	12	13	-	5	11	

Table 6 Repeatability r and Reproducibility R in the three Round Robin tests.

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