VAISALA

Study Committee D1

Materials and Emerging Test Techniques

Paper D1-PS1-10951

Determination of Gas Solubility for Dissolved Gas Analysis (DGA)

Senja LEIVO, Mikko ARONNIEMI, Sami VIRTANEN, Jarkko LARKIO, Toni MELLIN, Lydia HYRSKY, Sutidara NOPAKUN-BOROVSKA

Vaisala Oyj, FINLAND

Motivation

- Dissolved gas analysis (DGA) is a key method for condition assessment of transformers in service. It is based on fault gas concentration analysis of the insulation liquid.

- Gas concentrations are predominantly measured from a gas phase surrounding the oil sample, but results reported in the oil phase concentrations, i.e. microliter of gas in a liter of oil or parts per million (ppm).

- Obtaining gas concentrations in oil, thus requires a conversion from gas phase concentrations, using partition coefficients that relate oil and gas phase concentrations to each other.

- Solubility of different gases is affected by various parameters such as oil temperature and chemical composition of the oil.
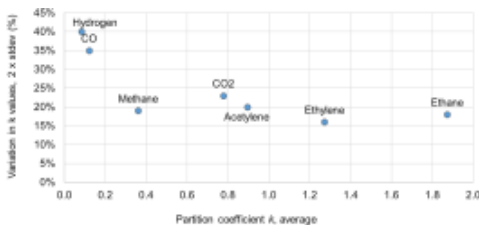

FIGURE 1: LITERATURE DATA OF THE PARTITION COEFFICIENTS OF DGA GASES (N=18) [1-6]. THE UNCERTAINTY REFERS TO THE VARIATION IN THE VALUES REPORTED.

- The interpretation of the gas concentrations and fault diagnosis results can be affected by uncertainties in partition coefficients.
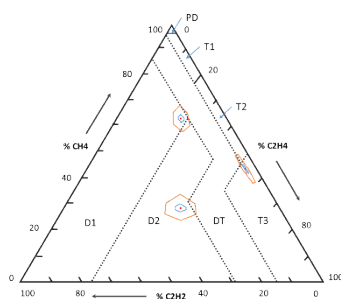

FIGURE 2: DGA DIAGNOSTICS TOOL, DUVAL'S TRIANGLE [7]. THE COLORED CONTOURS REPRESENT THE UNCERTAINTIES CORRESPONDING TO VACUUM EXTRACTION IN LABORATORY (RED), PARTIAL VACUUM EXTRACTION WITH AN ON-LINE MONITOR (BLUE), AND HEADSPACE METHOD (BROWN).

Objects of investigation

- How the oil-specific solubility of gases, namely partition coefficients k, can be determined in a laboratory with phase ratio variation (PRV) and headspace vapor phase calibration (HS-VPC) methods.

- Evaluation of the reproducibility of these two methods.

- Effect of gas concentration levels on partition coefficients.

Method/Approach

- In the phase ratio variation (PRV) method [8], the gas-in-oil sample is split into equal volume vials, but with different gas to oil volume ratios in each.

- Varying the gas-to-oil phase ratio allows one to calculate k from the slope intercept equation.
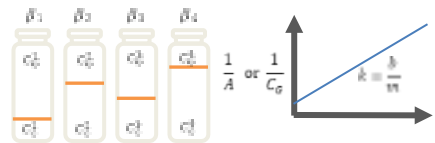

FIGURE 3: ILLUSTRATION OF THE PRINCIPLE OF THE PHASE RATIO VARIATION (PRV) METHOD.

- In the headspace vapor-phase-calibration (HS-VPC) method, an oil sample is bubbled to have equilibrium with a gas with known concentrations. Some oil is transferred into a vial, and its headspace concentrations are determined. Solubility coefficients can be calculated using concentration differences of the oil sample and the gas used for bubbling.
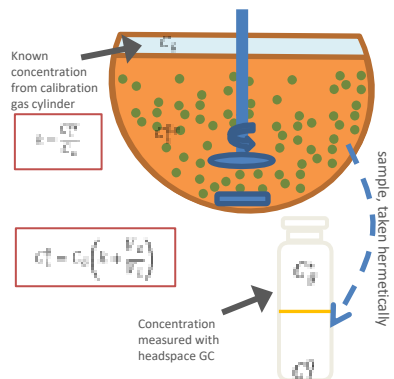

Known concentration from calibration gas cylinder

Concentration measured with headspace GC

sample, taken hermetically

FIGURE 4: ILLUSTRATION OF HEADSPACE VAPOR-PHASE-CALIBRATION (HS-VPC) METHOD.

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- The HS-VPC used is a modified method from the original vapor phase calibration (VPC) method, where a known gas concentration is injected to a vial and the gas solubility is determined by comparing the initial gas concentration to gas concentration in the gas phase after equilibrium has been achieved [8].

Experimental setup

- Using the PRV and HS-VPC methods, partition coefficients k for the 7 fault gases were determined at +60 °C for some new and used transformer oils and compared to k values of a widely used commercial gas-in-oil standard.

- For the PRV method 10–12 samples with different phase ratios were used to reduce the measurement uncertainty and to enable better statistical evaluation. Samples were inserted into the gas chromatograph (GC) at random order to minimize possible drift effects in the GC measurements.

- Gas concentration dependencies of the partition coefficients were studied with several oil samples having the gas mixture of methane, ethane, and ethylene with varying concentrations between 500 ppm and 50 000 ppm using nitrogen as balance gas.

Results

- Figure 5 shows an example of how the partition coefficient k was defined, using the PRV method and intercept equation for ethane, in one of the oils.

$$y = 0.0069x + 0.0133$$
$$R^2 = 0.9998$$
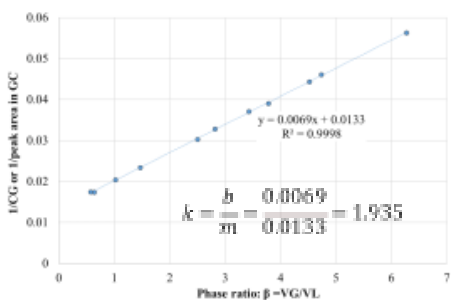
$$k = \frac{b}{m} = \frac{0.0069}{0.0133} = 1.935$$

FIGURE 5: EXAMPLE OF A LINEAR GRAPH WITH A GAS CHROMATOGRAPH SIGNAL (I.E. GAS PHASE CONCENTRATION) AS A FUNCTION OF PHASE VOLUME RATIO OF ETHANE GAS IN THE SAMPLE VIALS.

- Table 1 shows the determined partition coefficients for the fault gases in the gas-in-oil standard (Voltesso 35).

TABLE 1: PARTITION COEFFICIENTS OF THE FAULT GASES DETERMINED FOR THE GAS-IN-OIL STANDARD AT +60°C (VOLTESSO 35).

Gas	CH_4	C_2H_4	C_2H_2	C_2H_6	CO_2	CO	H_2
k	0.36	1.31	0.92	1.91	0.76	0.12	0.06

- Figure 6 and Figure 7 show the partition coefficient values determined for different mineral insulation oil samples in this study. To make comparison easier, the values are reported relative to those of the gas-in-oil standard shown in Table 1.
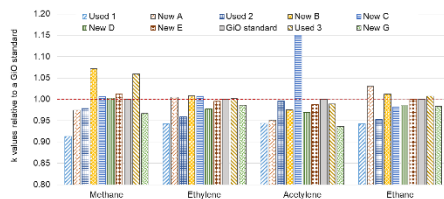

FIGURE 6: K VALUES DETERMINED WITH PRV METHOD RELATIVE TO THE GAS-IN-OIL STANDARD (GIO).
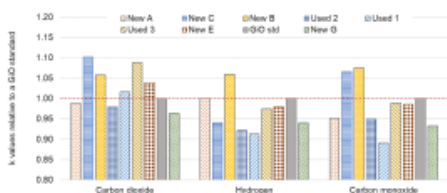

FIGURE 7: K VALUES DETERMINED WITH HS-VPC METHOD RELATIVE TO THE GAS-IN-OIL STANDARD.

- The effect of gas concentration on the partition coefficients is presented in Figure 8.

- To account for the difference between the solubility of each gas and to make the comparison easier, the determined k values at higher concentrations were normalized by comparing them to the k values determined at the 500 ppm concentration of each gas, respectively.
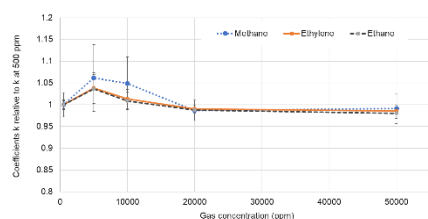

FIGURE 7 THE VALUES OF PARTITION COEFFICIENTS FOR METHANE, ETHANE, AND ETHYLENE AT VARYING CONCENTRATIONS RELATIVE TO K VALUES DEFINED AT 500 PPM WITH UNCERTAINTY DISPLAYED AS ERROR BARS

- No statistically significant change in k values at higher concentrations was observed.

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- Reproducibility for the analyzed gases were determined for both methods by repeating each method on 8 separate days. The results can be seen in Table 2.

TABLE 2: REPRODUCIBILITY OF PRV AND HS-VPC METHODS

PRV method reproducibility with the sample size of 8 (n = 8)

Compound	Average partition coefficient, k	Standard deviation x 2	Relative standard deviation, %
CH_4	0.373	0.038	10
C_2H_4	1.294	0.061	5
C_2H_2 (n=7)*	0.891	0.048	5
C_2H_6	1.911	0.095	5
CO_2	0.877	0.098	11
H_2	0.048	0.032	68
CO	0.125	0.043	34

HS-VPC method reproducibility with the sample size of 8 (n = 8)

Compound	Average partition coefficient, k	Standard deviation x 2	Relative standard deviation, %
CH_4	0.348	0.014	4
C_2H_4	1.096	0.074	7
C_2H_2	0.764	0.115	15
C_2H_6	1.366	0.552	40
CO_2	0.721	0.053	7
H_2	0.062	0.002	3
CO	0.124	0.006	5

Discussion

- For all gases and oils, the partition coefficients k were mostly within ±10% when compared to the gas-in-oil standard k values.

  - This is a significantly smaller uncertainty than what was determined when collecting and comparing the coefficient values from the literature.

  - We estimate that one main contributor for clearly lower uncertainties was that the coefficients for all oil samples were determined using the same methods.

- The PRV method showed good reproducibility for gases with partition coefficients of about 0.5 and higher. Gases with small coefficients such as hydrogen and carbon monoxide showed a large deviation in the reproducibility results.

  - The reason for this is probably that due to low solubility almost all hydrogen and carbon monoxide was in the gas phase which means that variation in volume ratios changed the GC signal only by a small amount.

  - For this reason, the HS-VPC method is considered preferable for analyzing gases with small partition coefficients.

- HS-VPC method reproducibility analysis showed the opposite: The method has good reproducibility for gases with small partition coefficients, but large relative deviation for the coefficients larger than about 0.5. The root cause for this is the inherently poor sensitivity of this method for large partition coefficients.

- For carbon dioxide, the PRV method showed a larger deviation in reproducibility when compared to HS-VPC, even though its partition coefficient was around 0.8. This is possibly due to small amounts of ambient carbon dioxide leaking into the vials at some point in the sample preparation. This offset would affect the samples with small oil volumes more, so it is possible that this changes the slope and intercept of the acquired linear fit curve.

Conclusion

- The use of coefficients picked from the literature may cause significant error in DGA results, if the oil to be studied has different partition coefficients or analysis conditions vary, especially when the headspace method is used for gas extraction from the oil sample.

- The results showed that while neither PRV or HS-VPC method alone is reliable for all the fault gases, by using both methods, it is possible to get accurate results for all fault gases.

- The results suggest that HS-VPC method is used for gases with partition coefficients under about 0.5 and PRV for those with higher partition coefficients.

- The PRV method is often more convenient, as accurate information on the gas concentrations in the oil is not needed in the analysis, but sample homogeneity is especially important in this method.

- Gas concentration level was not observed to affect partition coefficients in oil significantly or at least not at concentrations relevant to transformer application.

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