High-precision density sensor for concentration monitoring of binary gas mixtures

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Abstract

We developed an in-situ multi-sensor system for measuring the composition of a binary gas mixture. The sensor system simultaneously measures pressure, temperature and density from which the partial pressure of the individual gas components can be deduced and monitored online. In order to achieve highly precise measurements, the key component of the system, a microcrystal density sensor, is temperature-compensated enabling an error reduction of more than one order of magnitude. We show application of the sensor system for the exemplary case of monitoring binary mixtures in gas-insulated electrical installations and demonstrate that our measurement system achieves a concentration determination accuracy of better than $|\Delta c| < 0.5\%$-points.

Keywords: Gas mixture; gas concentration; mixing ratio; density sensor; microcrystal sensor; tuning fork; quartz resonator; SF$_6$ monitoring; SF$_6$/N$_2$; SF$_6$/CF$_4$; gas-insulated; GIS; GIL

1. Introduction

The knowledge of concentrations in binary or more complex fluid mixtures is of great importance in various industrial areas, such as gas monitoring in high-voltage gas-insulated equipment [1], metal-organic precursor delivery in semiconductor deposition processes [2], natural gas analysis [3] and fuel blending in petrochemical industry [4], gas polymerization processes [5] and for respiratory control in medical applications [6]. Diagnostic instruments like gas chromatographs, mass spectrometers or infrared spectroscopes are highly accurate and gas-specific, but often do not meet requirements because of high cost and intensive maintenance. Simpler and universal solutions (i.e., non-specific) are in many cases

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more desirable and often more straightforward to implement as a plug-on sensor system. Among such systems commonly used methods exploit the concentration-dependent speed of sound in acoustic resonator cavities [2,7] or they are based on resonant mechanical oscillators [1,5,8].

Here we describe the development and characterization of a measurement system using a mechanical oscillator (density sensor) combined with a pressure and temperature sensor. This \((pTp)-sensore\) system allows highly accurate determination of constituents of a binary gas mixture down to less than \(|\Delta c| < 0.5\%\)-points. The gas mixtures investigated, \(SF_6/N_2\) and \(SF_6/CF_4\), are common gaseous insulation fluids for low-temperature gas-insulated switchgear (GIS) and gas-insulated lines (GIL). In this equipment continuous gas concentration monitoring is required over long periods of time, since the dielectric strength of \(SF_6\) mixtures depends not only on the density but also on the mixing ratio and faults caused by e.g. leakage or condensation can change this ratio and thus compromise the proper operation.

2. Gas density sensing

A prerequisite for highly precise concentration readings with a \((pTp)\)-sensor system is a high density sensor accuracy which we realized by advanced temperature compensation. The density sensor consists of two microcrystal tuning forks, which are electrically excited to resonant oscillations. The fork with resonance frequency \(f_G\) is gas exposed, the other one sits in an evacuated reference cell and exhibits resonance frequency \(f_V\) (Fig. 1a).

Intrinsic temperature compensation is applied by monitoring the difference frequency \(\Delta f = f_G - f_V\) between the two forks. The relation between \(\Delta f\) and density \(\rho\) is described in [9]:

\[
\Delta f = A\rho + B\sqrt{\rho} + C = A\rho + B\sqrt{\rho}\eta(T) + C(T) \tag{1}
\]

where \(\eta\) is the \(T\)-dependent viscosity of the gas, \(A\) and \(B\) are functions of material and geometry constants of the quartz crystal, and \(C(T) = [f_{G,0} - f_{V,0}](T)\) with \(f_{G,0}\) and \(f_{V,0}\) representing the \(T\)-dependent vacuum resonance frequencies of gas exposed and reference fork, respectively. The difference frequency method cancels the dominating \(T\)-dependence, however, there are still remaining temperature influences. These are caused firstly by the \(T\)-dependent viscosity of the gas, and secondly by the small differences in the temperature dependence of the quartz material the two forks are made of. We analyzed these errors for pure \(N_2\) in a closed vessel of constant volume \(p = 4\) bar in a temperature range of \(-10^\circ C < \Delta T < 70^\circ C\) (Fig. 1b). The density calculated from Eq. 1 is plotted using a constant gas viscosity (squares) and using

![Fig. 1](image)

Fig. 1. (a) Quartz tuning fork sensor, metal-can package (left) and bare crystal with electrodes (right). (b) Density reading of a microcrystal sensor with (diamonds) and without (squares) temperature compensation. The solid lines are linear fits. The dashed-dotted line indicates the true density in the vessel. (c) Gas pressure vessel (\(V = 3.6\) dm\(^3\)) with three \((pTp)\)-sensor systems.
the $T$-dependent gas viscosity (diamonds). Our measurements using literature data of $\eta(T)$ [10] agree well with theory [9]. By taking the $T$-dependent viscosity into account, the relative density error can be reduced by more than a factor of ten, from $\Delta \rho/\rho = 3.8\%$ to $\Delta \rho/\rho = 0.3\%$.

3. Concentration determination in binary gas mixtures

As outlined above an easy solution enabling the determination of the concentration of the two gas components of a binary gas mixture involves measuring the gas pressure, temperature and density [1]. The partial pressure $p_A$ and $p_B$ of a two-component gas of pressure $p_{\text{tot}}$, temperature $T$, density $\rho$ and molar masses $M_A$ and $M_B$ is given by the following equations:

\[
p_A = \frac{RT}{M_A} \frac{p_{\text{tot}} - \rho M_B}{1 - \frac{\rho M_B}{M_A}}, \quad p_B = \frac{RT}{M_B} \frac{p_{\text{tot}} - \rho M_A}{1 - \frac{\rho M_A}{M_B}}, \quad (2a), (2b)
\]

using the ideal gas law ($pV_m = RT$) and Dalton’s law ($p_{\text{tot}} = p_A + p_B$). $R$ represents the universal gas constant and $V_m$ is the molar volume. From $p_A$ and $p_B$ the concentrations $c_A = p_A/p_{\text{tot}}$ and $c_B = 1 - c_A$ can be derived. We have constructed a ($pT\rho$)-sensor system with the aim of investigating the achievable concentration measurement accuracies for monitoring of SF$_6$/N$_2$ and SF$_6$/CF$_4$ mixtures in GIS. If concentration accuracies on the order of $\Delta c_B = \pm 1\%$ must be achieved, which is desirable for meaningful monitoring, primarily the performance of the density sensor is critical, since the density measurement uncertainty dominates the concentration error. A challenge resides in the large temperature range over which the measurement accuracy must be maintained and which becomes particularly pronounced through the temperature dependence of the density sensor (see section 2).

4. Experiments

The developed ($pT\rho$)-sensor system comprises a pressure sensor (Keller PAA-33X), a density sensor (Trafag 8774) and a temperature sensor (Heraeus, Pt100 M222, 1/3B). Three ($pT\rho$)-sensor systems were mounted on/in a pressure vessel (Fig. 1(c)) that was filled with binary gas mixtures (SF$_6$/N$_2$ and SF$_6$/CF$_4$). Each density sensor was pre-calibrated with pure SF$_6$ at $T=25^\circ$C using the ($p,T$)-readings of the system combined with the van-der-Waals equation for SF$_6$. To determine the impact of temperature on the measurement accuracy, the pressure vessel was exposed to various set temperatures in a $T$-controlled chamber. The thermal equilibration time for each temperature was approximately 6 h. A total pressure of around 6 bar was applied. The data of the three ($pT\rho$)-sensor systems was logged and the concentrations were computed online using the ideal gas equation for SF$_6$/N$_2$ (Eqs. 2a,2b) and the van-der-Waals equation for SF$_6$/CF$_4$ (see below).

The results for two binary mixtures of SF$_6$/N$_2$ and SF$_6$/CF$_4$ are shown in Fig. 2. The nominal concentrations of SF$_6$ were $c_B = 19.27\%$ and $c_B = 52.6\%$, respectively (indicated by the dashed horizontal lines in the plots). The concentration data shown include a linear correction for the temperature-dependent viscosity of the gas mixture. The ideal gas approximation is used for the mixture SF$_6$/N$_2$ and leads only to small errors in the concentration determination on the order of $\Delta c_B / c_B = \pm 1\%$ which is less than the residual errors. For SF$_6$/CF$_4$ mixtures, however, the deviation from ideality is larger and an appropriate equation of state for the gas mixture must be employed. Here we used the van-der-Waals equation combined with a formalism allowing the representation of a gas mixture [11]. From Fig. 2 it is evident that the measured concentration is correct to within $|\Delta c_B| < 0.5\%-\text{points}$ over a large temperature range.
Fig. 2. Concentration measurements of SF$_6$/N$_2$ and SF$_6$/CF$_4$ made with three different (pT)-sensor systems (circles, squares, triangles). The horizontal dashed line indicates the nominal SF$_6$ concentration.

The small residual temperature dependencies are a result of the linear correction and/or incomplete T-compensation of the pressure sensor and density sensor specific variations in the term $C(T)$ of Eq. 1.

In conclusion, the results demonstrate that our developed measurement scheme can be successfully applied using commercially available off-the-shelf sensors. To achieve highly accurate concentration readings two straightforward correction means are employed: (i) linear correction of viscosity-induced effects and (ii) pre-calibration of the density sensor. This concept permits high accuracy, low-cost concentration measurements of binary gas mixtures over broad operational temperature ranges for a multitude of industrial applications.

References