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Investigating the Variation of Thermal Conductivity with Temperature to Improve a Portable GC System Specificity

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Summary:
The variation of thermal conductivity with temperature for gaseous species is studied here to investigate if an improvement of the specificity can be achieved with a field TCD-based gas chromatography system. However, theoretical predictions as well as experiments indicate that the necessary local analyte concentrations are by far (two orders of magnitude) beyond the typical concentrations encountered by portable trace analyzers.

Keywords: gas, sensor, thermal, conductivity, detector

Background, Motivation and Objective

In the context of field gas chromatography (GC), a peak might be difficult to identify if two potential components elute at very close retention times. In the case where the sensor is a TCD, we propose to investigate if operating the sensor at different bias voltages could bring some kind of specificity to the portable system.

Description of the System

Thermal Conductivity Detectors (TCD) are universal sensors [1], whose working principle relies on the emergence of a thermal imbalance between membranes located in a reference channel (pure carrier gas) and membranes located in the analytical channel (carrier gas + analyte). The final membrane temperature itself originates from the competition between its heating by Joule effect (supplied electrical power) and its cooling through the surrounding gas (dissipated power via diffusion). Any emergence of a TCD signal is therefore the signature of the presence of a gas with a thermal conductivity λ different from the carrier gas thermal conductivity.

The thermal conductivity of any compound varies as a function of temperature according to its own law $\lambda(T)$, therefore it should be possible to introduce some kind of discrimination when interrogating the gas at different temperatures.

Predictive approach

In the case of a binary gas mixture (trace analyte in a majority carrier gas), the TCD signal will be proportional to the analyte concentration and to the difference of thermal conductivities between analyte and carrier gas (here, Helium). In order to be independent on the concentration, the ratio of the TCD signal S_2 at a bias V_2 (leading to an equilibrium temperature T_2) to the TCD signal S_1 at a bias V_1 (leading to an equilibrium temperature T_1) contains a factor that is characteristic of the analyte A in presence:

$$\frac{S_2}{S_1} \propto \frac{(\lambda_{He} - \lambda_A)_{T_2}}{(\lambda_{He} - \lambda_A)_{T_1}}$$

In the case of neighbor compounds like C_{10} (decane $C_{10}H_{22}$), C_{11} (undecane $C_{11}H_{24}$) and cumene (isopropylbenzene C_9H_{12}), those ratios only differ by 0.3% when applying V_1 = 9V and V_2 = 15V for example. To be able to discriminate between such small differences in the ratios, the impact of the measurement noise (± 5µV taken as a realistic value) has to be negligible, which typically happens when the TCD signals are high, i.e. at high analyte concentrations. This is illustrated by the convergence of curves when the analyte concentration increases locally (see Fig. 1). Only when the analyte concentration exceeds a certain value (red vertical bar), can the compounds be unambiguously discriminated: around 5%vol local concentration at the TCD membranes.

Experimental approach

In order to corroborate the predictive approach, an experimental set-up was implemented (see Fig. 2). In practice, we used two in-house fabricated TCD chips [2] (with a unique membrane design) biased at two different voltages V_1 and V_2 (respectively 3V and 9V), but we could also

have used a unique TCD sensor successively biased at V_1 and V_2.

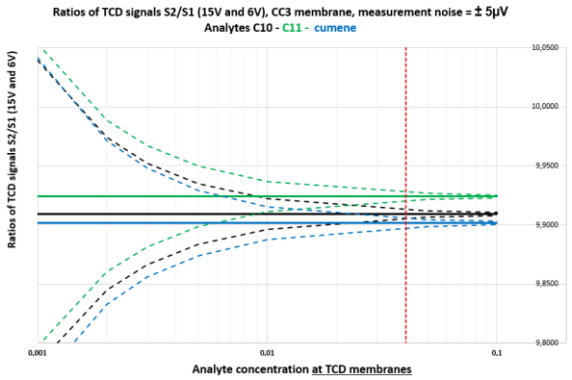

Fig. 1. Graph of predicted ratios of TCD signals (S2/S1) vs analyte local concentration for three different compounds (horizontal lines: theoretical values; dotted lines: when introducing measurement noise).

A gaseous mixture of BTEX (Benzene, Toluene, Ethylbenzene, o-Xylene at 10ppmvol or 500ppbvol) was injected via a rapid desorption of a Silicon pre-concentration chip [3], went through in the TCD reference channels, was separated by a chromatographic column (from Supelco SLB-5ms column, 5m long, ID 0.25µm, phase thickness 0.25mm), and went back in the TCD analysis channels.

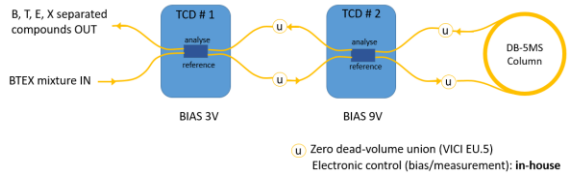

Fig. 2. Outline schematic of the experimental set-up (Silicon pre-concentration chip not represented).

The measurements were repeated several times to get representative statistics. Typical chromatograms are shown in Fig. 3.

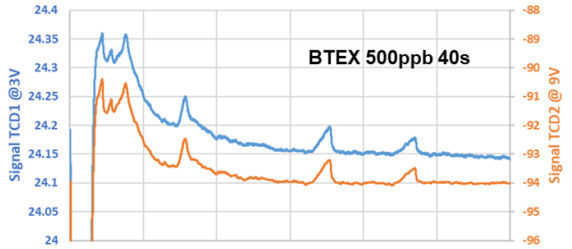

Fig. 3. Typical chromatograms obtained for the BTEX mixture analysis (TCD traces at two different biases 3V and 9V).

The ratios of TCD signals were plotted in Fig.4: the expected tendency is found, i.e. a convergence of the dots distribution (less spreading with increasing local analyte concentration).

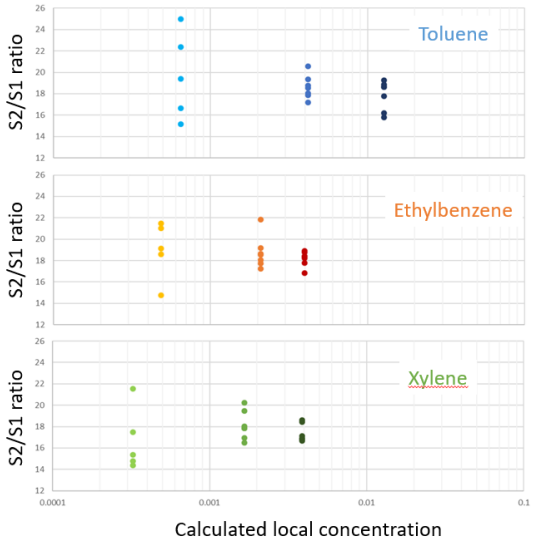

Fig. 4. Experimental ratios of TCD signals (S2/S1) vs analyte local concentration for three different compounds.

However, the measurement uncertainty remains too high to be able to distinguish the components on the only basis of S2/S1 ratios. Furthermore, the investigated concentrations here are beyond the usual scope of trace analysis (local range 300ppm to 1%vol).

Conclusion

In conclusion, it seems that the ratio of TCD signals at two different biases is not relevant for a doubt removal, when a potential identification confusion exists with two compounds eluting at the same retention time, because this approach would require working at high local concentrations (~ 5%vol). This prediction was confirmed experimentally with compounds eluting at distinct times: even at high local concentrations, (300ppm – 1%vol), the double measurement does not allow to clearly identify which compound is eluting, and such values are inadequate for a trace analyzer system.

Acknowledgements

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