

Development of UV-Ionization Based Trace Differential Mobility Sensor for Acetone and Hexane

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Abstract – Clinical studies in recent times confirm feasibility of using trace concentrations of volatile organic compounds (VOC) in human exhale air as potential bio-markers for a variety of disease states. A Differential Mobility Sensor (DMS) with dual ultra-violet (UV) photo-ionization source is proposed and demonstrated for measurement of trace amounts of VOC gases in human exhale air. Experimental work performed with the DMS using high frequency asymmetrical waveform field for detection of trace concentrations of acetone and hexane with a few carrier gases including air, CO₂ and O₂ is discussed. The detection limit as estimated for Signal to Noise Ratio (SNR) of 3 is of the order of sub ppm levels for acetone and hexane. Experimental studies clearly demonstrate selective sensing of a gas in a mixture of gases by applying appropriate compensation field. Preliminary study on sensing of acetone in human breath shows good a correlation with blood glucose measurements.

I. INTRODUCTION

The past decade has seen increasing interest in study of patho-physiological and metabolic processes in human body through compositional analysis of human exhaled air [1]-[5]. Certain clusters of volatile organic compounds (VOCs) in human breath are considered to serve as non-invasive biomarkers for various disease states such as hyperlipidemia, cancer, diabetes, kidney and liver disease, recent smoking behavior, etc [5]. Clinical analysis of VOCs in human breath show acetone concentrations in the range 2 to 1000 ppm for diabetics [2], hexane of the order of 10 ppm or greater in conjunction with abnormally high levels of other associated VOCs is suggestive of lung disease such as tuberculosis and nerve damage.

Trace gas detection techniques such as Proton-Transfer Reaction Mass Spectrometry (PTR-MS), Gas Chromatography Mass Spectrometry (GC-MS), Selected-Ion Flow-tube Mass Spectrometry (SIFT-MS), Tunable Diode Laser Absorption Spectroscopy (TDLAS), Cavity Ring-Down Spectroscopy (CRDS) have been reported for

investigations for human breath analysis [2]-[6]. However, these methods are expensive, bulky, requiring special installation environments and are not suited to large scale deployments. Studies undertaken for evaluation of VOCs as cancer bio-markers [5], by chromatography/MS through solvent extraction methods use solvents such as hexane, methanol, ethyl-acetate, etc. However, the use of solvents might result in alteration to possible detection of trace levels of the solvent VOCs in human breath.

Recently, superluminescent diodes with wavelength in optical communication band have been reported for measurements of NH₃ and water vapor [7]. The approach allows detection of multiple gas species but the wide range of VOCs has specific absorption bands in mid-infrared region (2 to 5 μ m). Ion Mobility Sensors (IMS) based on either Time-of-flight (TOF) or differential mobility (DMS) of ions in high and low electric fields for detection of trace VOCs for chemical warfare and explosives [8]-[13]. TOF-IMS chiefly relies on separation of ion species of different ion mobilities in an electric field within a drift-tube. The high field differential ion mobility method, also called Field Asymmetry Ion Mobility Spectroscopy (FAIMS), relies on separation of ions in high frequency asymmetric electric field waveform where gas ions are subject to alternate high and low electric fields. In this study, a novel miniature DMS sensor using UV light source for photo-ionization has been proposed and demonstrated for detection of trace VOC gases, namely acetone and hexane.

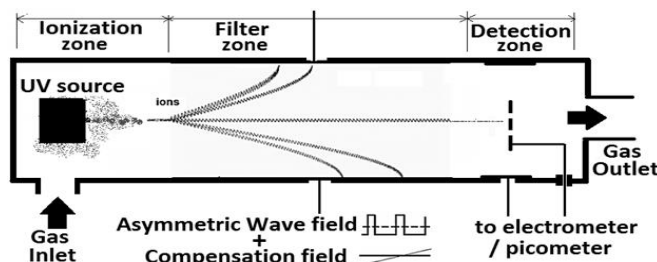


Fig. 1 Schematic of a FAIMS based DMS sensor

In a typical DMS sensor, as in Fig. 1, sample gas containing trace VOCs when introduced with carrier gas flow is first subject to ionization. Conventionally methods such as radioactive isotope (e.g. β -source Ni, α -source Am), corona-discharge, electro-spray ionization, etc., are used. This paper discusses a breath gas sensor utilising UV photo-ionization source, which enables selective ionization of VOC gases of interest in human exhaled air without affecting abundant gases such as N₂, O₂, etc. The VOCs with ionization energy

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less than energy of UV source (10.6 eV) are ionized and post ionization, ions with neutral molecules of carrier gas flow through ion filter zone. At the filter zone ions are subject to high frequency (~1 MHz) asymmetric electric field (E_F) as applied using a pair of non-corroding electrodes. The ions with carrier gas subsequently flow down to detector zone where an electrode pair detects the ions.

Gaseous ions exhibit difference in their ion mobility in strong and weak electric fields. During each cycle of E_F , ions experience a short period of extremely high field followed by a larger period of low strength electric field in reverse direction. The DMS waveform typically has 25-35% duty ratio with unequal amplitudes for positive and negative going half-cycles. A low amplitude DC compensating field (E_C), of either polarity is applied to filter electrodes in conjunction with E_F to tune the filter to selectively enable detection of specific ion species. The differential mobility for various ion specie result in separate trajectories for each ion species when subject to E_F with E_C and thereby cause separation of ions.

The ion mobility at high electric field (~10 kV/cm or greater) is a function of applied field (E) and inversely related to gas density (N) [9], [10] as given by,

$$K\left(\frac{E}{N}\right) = K_0 \left[1 + \alpha \left(\frac{E}{N}\right)\right] \quad (1)$$

where, $\alpha \left(\frac{E}{N}\right)$ is electric field dependency of ion mobility and K_0 is low field mobility constant. Different ions have different alpha characteristics $\alpha \left(\frac{E}{N}\right)$ and ion-mobilities.

During motion of ions and neutral molecules in an electric field, velocity of ion drift in the direction of field is given by [10]

$$\bar{v} = K\left(\frac{E}{N}\right) \bar{E} \quad (2)$$

The transverse motion of ions under influence of electric field yields a trajectory specific to each ion species as dictated by expressions (1) and (2). The transverse displacement is therefore the integral of instantaneous ion velocity and time instance. Ions with total transverse displacement less than filter electrode gap-width are carried to the detector by carrier gas flow while all other ions collide with filter electrodes and become neutral.

In this work, a UV-Photoionization based DMS Sensor is designed and manufactured. The VOCs- acetone and hexane, as well as mixtures of acetone-hexane in trace concentrations is investigated using the DMS sensor. Experiments were conducted using different carrier gases such as air, CO_2 and O_2 .

II. EXPERIMENTAL INVESTIGATIONS

A. Ion Mobility Sensor prototype

An Ion mobility sensor, as shown in Fig. 2, was designed to handle gas flow rates in the range 1 to 10 litre

per second (lpm). A prototype sensor constructed in Teflon material, and with Ionization zone comprising of two UV lamps (10.6 eV/ Heraeus NobleLight PKR-106). VOCs such as acetone (9.69 eV) and hexane (10.13 eV) are ionized by the UV source. The filter-zone has a pair of planar electrodes spaced 400 μm apart while the detector is a pair of concentric electrodes. The dual UV based DMS sensor is shown in Fig. 3.

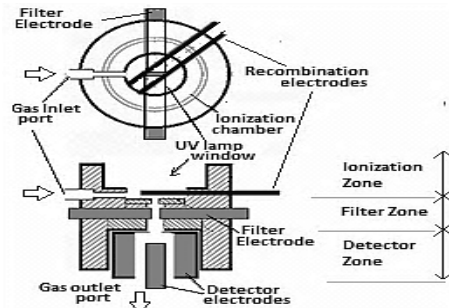


Fig. 2 showing schematic of DMS used in the study.

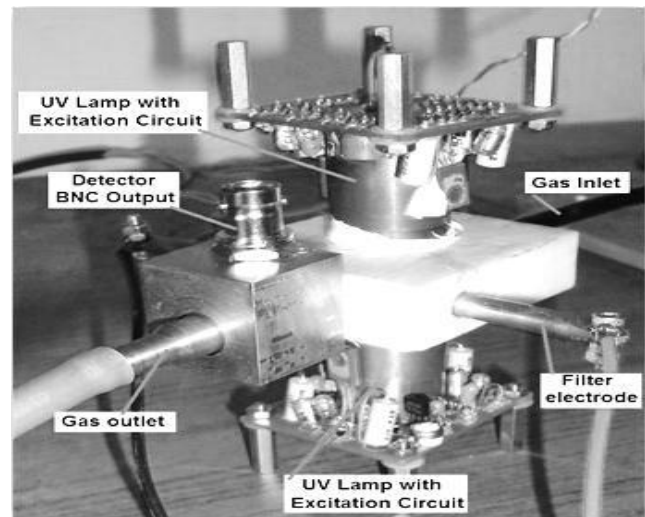


Fig. 3 showing position of dual UV sensors in the DMS sensor.

B. Investigations on Ion Mobility Sensor

The test setup used for experiment work (as shown in Fig. 4) comprises of regulated supply of pure carrier gas through a mass-flow controller. The gas is sent through an apparatus comprising pairs of U-tube bubbling columns filled to about 50% with VOC liquids acetone and hexane. When gas is bubbled through any U-tube, it carries volatile vapour into the downstream DMS sensor.

The instrumentation comprises of Waveform Generator (Agilent 33120A), wideband amplifier (Krohn-Hite 7602M), Digital Multimeter (Keithley 1200), picoammeter (Keithley 6485), programmable voltage source (Yokogawa CA100) and associated accessories. A rectangular waveform of 1 MHz and of fixed amplitude and duty ratio is sourced from waveform generator to wideband amplifier. The amplifier gain and offset are adjusted to generate E_F . A DC voltage driven to its second input after

amplification is the V_C . A pico-ammeter connected to detector is used to measure ion current. Experiments were conducted for 1 MHz asymmetric rectangular-wave with 33 % duty-ratio for moderate high and low electric fields of amplitude 1333 V/cm and 666 V/cm, respectively. During the tests, rate of vaporization as determined by observing rate of volume depletion and the actual carrier gas flow indicates concentration of VOC flowing into DMS.

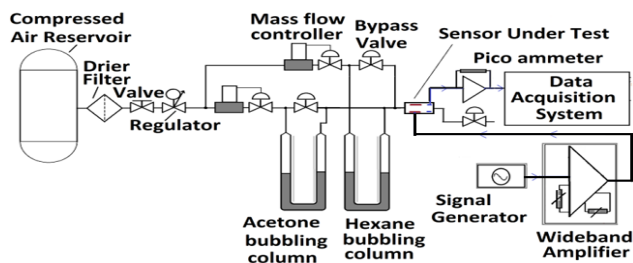


Fig. 4 Schematic of Experimental setup and Instrumentation used for testing FA-IMS Sensor.

During the tests, for a controlled carrier gas flow and a desired rate of bubbling in U-tubes, the digital output from pico-ammeter is acquired directly to a Data Acquisition system. Measurements are recorded with flow of carrier gas as well as with trace VOC in carrier gas, to evaluate detectable change in ion current at the picoammeter.

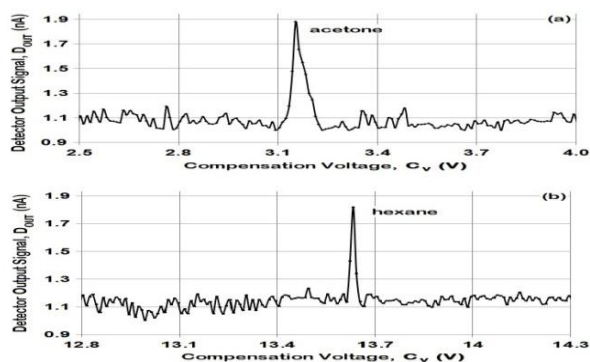


Fig. 5 D_{OUT} signal peak of FA-IMS after compensating for carrier gas for detection of (a) acetone, (b) hexane at flow of about 22 m/s.

To evaluate the performance of DMS sensor for detection of acetone in human breath, breath exhalate was collected from volunteers in sample-bags and fed into the sensor. Using a glucometer (Make ORSENSE/Model Glucogard), the blood glucose levels for the volunteers were also recorded when collecting breath gas samples. The gas sample was evaluated for detection of acetone.

III. RESULTS AND OBSERVATIONS

The DMS sensor shows a V_C of 3.1 VDC for E_F of 1 MHz 33% duty-ratio rectangular wave as measured for gas flow of about 2 lpm (~20.8 m/s). The detector output (D_{OUT}) corrected for charge measured with neutral carrier gas (air) and measured at various V_C over the range -40 VDC to +40 V DC is shown in Fig. 5 for acetone and hexane respectively. Distinct output peaks are observed for V_C at

about 3.13 V and 13.63 V respectively for acetone and hexane are observed.

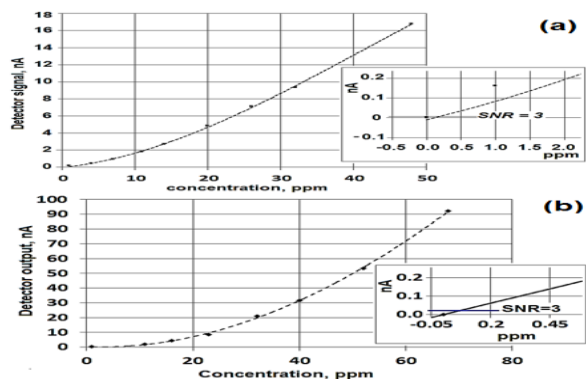


Fig. 6 Detection D_{OUT} for (a) acetone, (b) hexane with Insets showing detection at SNR of 3.

The detector output D_{OUT} at detection peaks as measured on pico-ammeter for acetone and hexane at different concentrations are measured. The D_{OUT} varies proportionally with change in concentration as shown in Fig. 7. The D_{OUT} analyzed for signal-to-noise ratio (SNR) yield an estimate for limits of detection of the order of 70 to 100 ppb for both acetone and hexane. The detection limits are comparable to detection values in literature [11].

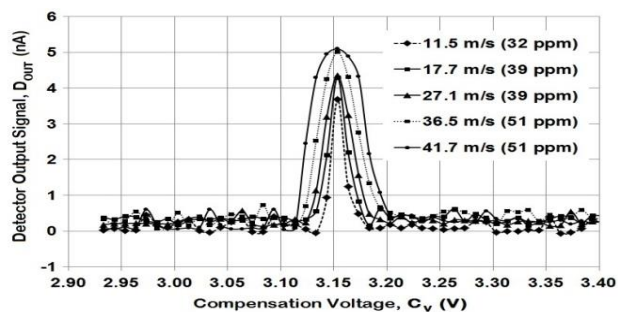


Fig. 7 V_C peak determined for acetone at different flows.

The effect of variation in flow on V_C peak is studied experimentally, as shown in Fig. 7. This is along expected lines since for given asymmetric wave frequency, the number of cycles of ion oscillations in asymmetric field in filter zone depends only on gas velocity. Net ion drift in transverse direction towards filter electrode increases when ion is subject to larger number of oscillation cycles. Therefore, higher gas velocity yields broader peaks compared to peaks with lower gas velocity

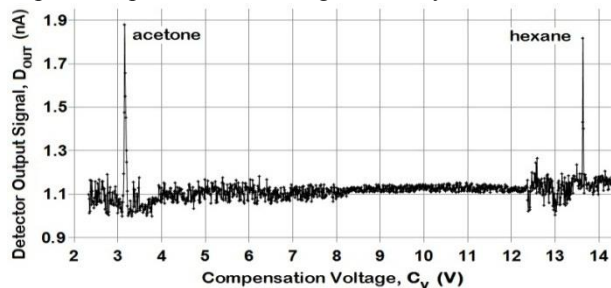


Fig. 8 Detection for acetone-hexane mixture (12 ppm) with air as carrier gas for single UV based DMS sensor.

Experiments were also conducted to evaluate performance of DMS sensor for detection of acetone-hexane mixture. Fig. 8 shows V_C peaks at around 3.13 V and 13.63 V representing acetone and hexane during experiments with acetone-hexane mixture.

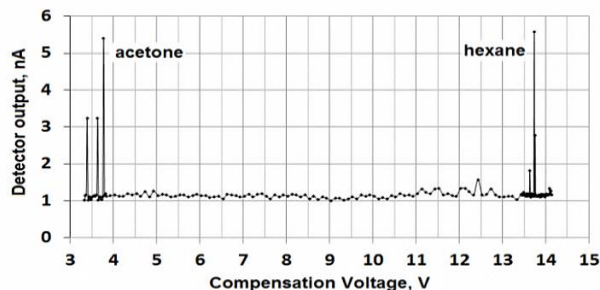


Fig. 9 Detection for acetone-hexane mixture (20 ppm) in CO_2 as carrier gas for dual UV based DMS sensor.

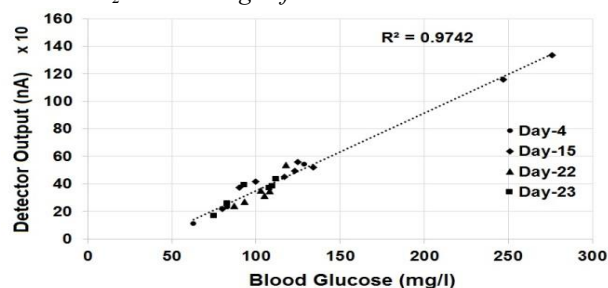


Fig. 10 Detection of acetone in human breath against blood glucose measurements.

Experiments for detection of acetone and hexane with O_2 as carrier gas indicate no change in V_C compared with air as carrier, while in case of CO_2 as carrier gas, slight shift in detection peaks for acetone and hexane detections were observed at 3.77 V and 13.73 V, respectively. There is however no change in detection limits with O_2 or CO_2 as carrier gas. The results of tests performed for detection of acetone in human breath from a few volunteers are shown in Fig. 10. The plot represents readings corresponding to detection based on proposed sensor and the glucometer. The observations made on different days are represented by different legends. A linear fit was obtained between proposed sensing technique and blood glucose measurements with regression coefficient value of approximately 0.97.

IV. CONCLUSIONS

Experimental studies were conducted on a compact UV-Photo-Ionization based Asymmetric Field Differential Ion Mobility Sensor (DMS) developed in-house. Experiments were performed with air, O_2 and CO_2 as carrier gases. The Sensor shows detection of the order of 70-100 ppb for acetone and hexane as estimated from Signal to Noise Ratio of 3. Experiments confirm detection of acetone and hexane from acetone-hexane mixtures with air, O_2 and CO_2 as carrier gases although there is a shift in compensation voltage for CO_2 as carrier. It also confirmed that there is no change in compensation voltage with

variation in carrier gas velocity. Preliminary tests on breath gas samples confirm a linear correlation (regression coefficient approximately 0.97) between proposed DMS sensor and blood glucose measurements.

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