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Accuracy and cross-sensitivity analysis of the PMS5003 formaldehyde sensor

Karolina Brończyk, Michał Adamski,
Agata Dąbrowska
Department of Trace Analysis, Faculty of Chemistry
Adam Mickiewicz University
Poznań, Poland
{karbro3, michal.adamski, agatadab}@amu.edu.pl

Adam Konieczka, Adam Dąbrowski
Division of Electronic Systems and Signal Processing
Institute of Automatic Control and Robotics
Poznan University of Technology
Poznań, Poland
{adam.konieczka, adam.dabrowski}put.poznan.pl

***Abstract* — Measurement data produced with the PMS5003 electrochemical sensor, allegedly selective for formaldehyde, were analyzed. The amounts of formaldehyde released from heated standard solutions were measured. At the same time, samples were sorbed into sorption tubes with an XAD-2 cartridge, which enabled chromatographic analysis – gas chromatography coupled with an electron capture detector (GC-ECD). A susceptibility of the PMS5003 sensor to cross-sensitivity associated with the presence of other low-molecular-weight carbonyl compounds, such as acetaldehyde and acetone in the sample, was also tested. The conducted research clearly indicates poor selectivity/accuracy of the PMS5003 sensor in relation to formaldehyde and its sensitivity to the presence of other carbonyl compounds in the sample, with a structure similar to formaldehyde.**

Keywords* — *formaldehyde; carbonyl compounds; PMS5003 electrochemical sensor; cross-sensitivity; chromatographic analysis

I. INTRODUCTION

Formaldehyde (FA) belongs to low molecular weight carbonyl compounds with the formula HCHO. It is classified as a ubiquitous compound in the environment, and the sources of its formation can be divided into natural and anthropogenic. The natural presence of this compound in the environment is related to the phenomena of photochemical processes, the decomposition of natural organic matter, and the life processes of plants and animals. FA molecule is bioactive, responsible for demethylation processes. It is also a secondary metabolite of plants. FA can also be easily leached out of the troposphere and get into surface waters with precipitation (rain, snow) [1, 2].

Anthropogenic sources of FA in the environment include popularly used water disinfection processes (chlorination, ozonation). FA is a product of the oxidation of organic matter by strong oxidants [3]. Degradation processes of plastics are also an important source of FA, and this compound may easily migrate to packaged food [4, 5]. Moreover, all combustion processes constitute a particularly important source of FA in the air, so the development of industry and urbanization may contribute to the identification of increasingly higher concentrations of this compound in the air [6, 7]. Additionally, FA is widely used in various industrial sectors, including the production of resins, antimicrobials and disinfectants, textile processing, pharmaceutical production, biomedical research, furniture and construction materials [8-10].

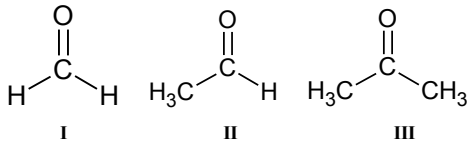
Identification of FA in the environment may be controversial due to its undesirable properties. According to the International Agency for Research on Cancer (IARC) and WHO, FA is classified as carcinogenic, mutagenic and allergenic compound [11, 12]. Previous research has shown that excessive exposure to FA may cause various diseases, e.g. problems with fetal development, chronic inflammation, cardiovascular diseases and leukemia [13, 14]. Therefore, the detection and monitoring of FA concentration levels in environmental samples is particularly important. Therefore the number of studies in this area is constantly growing.

There are many research methods enabling the detection of FA, and the most frequently used include: chromatographic methods, e.g. gas chromatography [15], high-performance liquid chromatography (HPLC) [16], spectroscopic methods, e.g. infrared spectroscopy [17], fluorescence spectroscopy [18]; Raman spectroscopy [19] and electrochemical methods [20, 21]. Each of these methods has unique features.

Chromatographic methods ensure separation of analyzed chemical compounds on a chromatographic column and high accuracy of results (they ensure separation of FA from compounds with similar structure). However, they require the use of stationary equipment and complex procedures for the initial preparation of samples for testing, which often limits the possibility of monitoring FA in real time. In turn, spectroscopic methods provide a fast reaction, but often require the use of derivatization molecules or fluorescent probes.

Electrochemical methods are the most promising, taking into account the labor-intensive, time-consuming and expensive nature of analyses. They enable quick measurement of FA concentration in samples, without the need to prepare samples for testing, design analyses, or purchase expensive chemical reagents and research equipment. Currently, there are many electrochemical sensors specific for FA. However, the limitations of such simple devices include low accuracy of indications and cross-sensitivity. Comparisons of the sensor data with the results obtained using reference methods, e.g. chromatographic methods, are carried out, in order to determine the accuracy of the electrochemical sensor data. In turn, the cross-sensitivity of

an electrochemical sensor involves a false over-reading, which is due to the presence of chemical compounds with a similar structure (mass) to the tested compound in the sample. For FA-specific electrochemical sensors, compounds causing cross-sensitivity can include acetaldehyde (AA) and acetone (Ac) (Fig. 1).



I II III

Fig. 1. Chemical formula of formaldehyde (I), acetaldehyde (II) and acetone (III)

The aim of the work was to determine the accuracy of indications and cross-sensitivity of a popular FA-specific electrochemical sensor (PMS5003). The FA concentration was electrochemically measured in a standard solution of precisely known concentration and the data from the sensor was compared with the results obtained using the reference chromatographic method: gas chromatography with an electron capture detector (GC-ECD). Additionally, the data of the electrochemical sensor was checked for acetaldehyde and acetone standard solutions, which allowed to determine the cross-sensitivity of the PMS5003 electrochemical sensor to the presence of carbonyl compounds with a structure similar to FA in the sample.

The paper is organized as follows. Section II presents popular HCHO sensors, their operating principle and parameters. Section III describes the reference chromatographic method (GC-ECD). Section IV presents the conducted experiment, obtained results and discussion. A short summary is provided in Section V.

II. HCHO ELECTROCHEMICAL SENSORS

There have been about 300 publications on FA sensors in the last decade. Current electrochemical techniques have many advantages, such as high sensitivity, selectivity and the possibility of real-time analysis, which make them highly effective for monitoring FA occurrence. Electrochemical FA sensors can be divided into two groups.

The first one includes solid-state sensors that mainly warn of the presence of FA. They are simple in design, compact and inexpensive. Their principle of operation is based on the reaction of FA molecules with adsorbed oxygen on the surface of semiconductor materials.

The second group includes electrochemical sensors based on solution reactions. These sensors primarily involve the chemical oxidation of FA on the electrode surface, resulting in a current or an electric potential response [8].

Currently, gas sensors based on a thin ZnO layer are very popular. The principle of their operation is a modification of the surface structure. During gas detection, a surface reaction occurs. The adsorption of gas molecules on a thin ZnO layer affects its conductivity. These types of sensors are characterized by a very high surface-to-volume ratio and excellent stability due to perfect crystallinity [22].

A disposable electrochemical sensor has also been developed for the rapid detection of FA gas. It consists of a three-electrode screen printing system modified with hydrazine polyacrylate. It serves as a center for FA accumulation/ derivatization and as a polyelectrolyte enabling voltametric measurements [23].

The cheapest FA-detecting sensors can be purchased for less than $7. One of these is the Grove – air purity sensor MP503 v1.3 [24]. According to the specifications it is used for detecting slightly toxic gases such as carbon monoxide, alcohol, acetone, thinner, FA, and others. It transmits measurement data in an analogue manner and its claimed sensitivity to many gases precludes its use for precise FA measurements. In a similar case, it is possible to purchase the Fermion: MEMS Formaldehyde HCHO Gas Detection Sensor – module with the formaldehyde sensor [25]. It is made using MEMS (microelectromechanical system) technology and allows measurements in detection range of 0 to 3 ppm. According to the manufacturer [26], this sensor only enables qualitative measurements and is not calibrated at the factory. However, no information is available on sensitivity to other gases. Four times more expensive is the Threshold Formaldehyde HCHO Sensor – HCHO concentration sensor [27], which is dedicated to measuring ambient air quality. It is used to detect whether the surrounding environment exceeds a set concentration threshold. It has an output in the form of a two-state digital signal. Its application could be systems that warn if indoor concentrations are exceeded. Also, there is no information on sensitivity to other substances such as alcohol or CO.

Manufacturers of more expensive sensors such as the Gravity: Formaldehyde (HCHO) Sensor – HCHO concentration measurement module [28] priced at $65 or the Grove Formaldehyde Sensor (SFA30) – HCHO concentration measurement module [29] priced at $89 claim that they measure HCHO concentration in the range up to 5 ppm with an accuracy of 0.01 ppm (Gravity Sensor). These sensors transmit data digitally using UART or I2C interfaces. Interestingly, both also come with a disclaimer about sensitivity to other gases.

Finally, the PMS5003 sensor with an FA probe, costing approximately $40, was selected to conduct these tests. The choice resulted from the fact that this sensor also measures the concentration of suspended dust PM1, PM 2.5 and PM10 as well as air temperature and relative humidity, which makes it a very useful element for measurement stations monitoring the quality of the atmospheric air.

According to the manufacturer data, FA effective range is: 0-1 mg/m³, maximum range: 0-2 mg/m³, resolution: 0.01 mg/m³. Declared FA maximum consistency error: 5%, working temperature range: from −10°C to 60°C [30].

III. REFERENCE METHOD – GAS CHROMATOGRAPHY

Gas chromatography with an electron capture detector (GC-ECD) is an analytical tool that enables the identification and quantification of FA in samples at low concentration levels (ng/l). Gas chromatography (GC) enables the separation of compounds characterized by high volatility and low molecular weight. Chemical compounds are separated based on differences in boiling points. In turn, the electron capture detector

(ECD) is a specific detector sensitive to compounds containing halogen atoms. The basic element of ECD is a source of β radiation, which is most often the radioactive isotope 63Ni. The electrons created by this radiation interact with nitrogen (ECD make-up gas), which causes the electron energy to decrease (base current is generated). The neutral analytical particles are introduced together with the carrier gas into the ionization chamber. Strongly electronegative atoms (e.g. fluorine) capture electrons flow in the electric field from the anode to the cathode. The formed anions (X-) move towards the electrode much slower. This causes collisions with nitrogen cations and recombination. Neutral particles of the analyzed compound leave the chamber together with the carrier gas. The analysis concentration is proportional to the decrease of the flowing current.

IV. EXPERIMENT

A measurement station was built to carry out the experiment (Fig. 2). It consists of a borosilicate glass jar into which 50 ml of standard solutions of FA, AA, and Ac were introduced. The concentrations of carbonyl compounds were: 985 µg/m^3 for FA, 1080 µg/m^3 for AA and 1005 µg/m^3 for Ac. The borosilicate jar was changed for each measurement to avoid secondary contamination. The jar was placed approximately 20 cm above an 800 W heater. In order to determine the cross-sensitivity of the PMS5003 sensor, each of the standard solutions of carbonyl compounds was heated to 35°C. The rising vapors were directed through a silicone tube with an internal diameter of 4 mm to the air inlet of the PMS5003 sensor. The air flow was forced by the sensor's internal fan. The sensor was connected to the ESP32-DevKitC-32D development board using the UART (Universal Asynchronous Receiver-Transmitter) interface. A waterproof probe with temperature sensor DS18B20 was also connected to this board. This probe was used to measure temperature into the jar. FA concentration measurements were made for 4.5 min every 5 seconds, after the temperature had stabilized.

Fig. 2. Measurement of HCHO concentration in a heated borosilicate glass jar; air tubes are visible at the top, the DS18B20 temperature sensor inside the jar, and the heater at the bottom

In order to assess the accuracy of the PMS5003 sensor data, chromatographic analysis was performed in parallel using GC-ECD. During the measurements, the vapors emitted from the heated FA standard solution were pumped onto the sorption tubes with the XAD-2 insert using an SC301P microvacuum pump (flow 112.8 ml/min), which operates in the voltage range of 2.5÷6 V. They required additional sealing with Teflon tape. Pumping into the sorption tube lasted 2 minutes from the moment the temperature of 35°C was reached. The adsorbed samples were subjected to preliminary preparation for GC-ECD chromatographic analysis. The procedure included derivatization, extraction, and purification, which was described in detail in our previous work [20]. FA was identified based on retention time (time of elution of the compound from the chromatographic column and appearance of a peak in the chromatogram) and quantified based on the calibration curve equation. The obtained limits of detection (LOD) and quantification (LOQ) for FA are low (ng/l), which confirms the high sensitivity of the GC-ECD method towards FA. The analytical data are presented in the Table I.

TABLE I. Formaldehyde with analytical data of the GC-ECD method.

Analyte	Retention time [min]	Calibration curve equation	LOD [µg/l]	LOQ [µg/l]
Formaldehyde	5.82	y=38x+2011	0.003	0.009
Actaldehyde	8.10; 8.24	y=57x+1343	0.005	0.015
Acetone	8.56	y=42x+20	0.020	0.060

V. ACHIEVED RESULTS

The obtained measurement data for the PMS5003 sensor are shown in Fig. 3. Based on the results, it is clearly visible that the PMS5003 electrochemical sensor (according to the manufacturer's declarations specific for formaldehyde) is characterized by a substantial cross sensitivity towards acetaldehyde and acetone. This is probably related to the similar structure (mass) of these compounds to formaldehyde, as presented earlier (Fig. 1). This means that the PMS5003 sensor incorrectly reads acetaldehyde and acetone as formaldehyde. In our previous work [20] we showed that the FA concentrations in campfire smoke and vapors from the exhaust pipes measured using the PMS5003 sensor are overestimated compared to the results of the reference GC-ECD method. The results of this work clearly indicate that the reason for these discrepancies is the presence of others carbonyls in the analyzed environmental samples, i.e. AA and Ac.

Moreover, different concentration correlations were observed for the analyzed carbonyl compounds throughout the measurement cycle (Fig. 3). In the case of FA, an increase in concentration was observed from the beginning of the measurements to approximately 150 seconds of measurements, after which the concentrations of this compound decreased. In turn, an increase in concentrations was observed for AA and Ac throughout the measurement cycle. These trends may be related to the different boiling points of these carbonyl compounds. FA has the lowest boiling point among the tested compounds (⊣9°C). Therefore, it evaporates the fastest (0-150 seconds of measurements) and thermally degrades (150-270 seconds of measurements). AA and Ac have significantly higher boiling points, which are 20.2°C and 56°C, respectively. AA, as a more volatile compound, is released from the heated solution faster than Ac, which can be seen in Fig. 3.

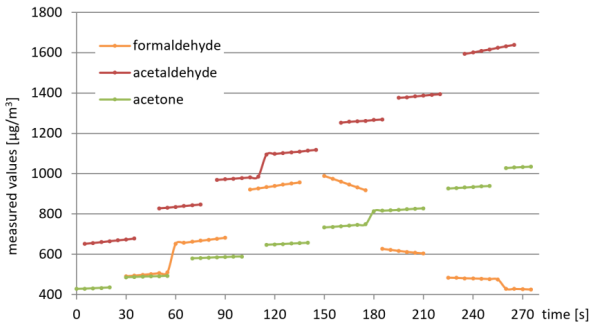


Fig. 3. The concentrations recorded by the sensor as a function of time (acetaldehyde and acetone incorrectly measured by the sensor as formaldehyde)

GC-ECD chromatographic analysis of the FA sample showed that the concentration of this compound adsorbed on the XAD-2 sorption tubes was 537 µg/m^3 (this result includes the flow of 112.8 ml/min, 112.8-fold sample concentration, and recovery of 75%). The average concentration indicated by the PMS5003 sensor was 686 µg/m^3 during pumping into the tube. The discrepancy in the results clearly indicates low accuracy of the PMS5003 sensor during measuring the FA concentration.

VI. Conculsions

The paper checked the cross-sensitivity and low accuracy of the data of the PMS5003 electrochemical sensor, which, according to the manufacturer, is specific for formaldehyde. Based on the obtained results, it can be concluded that the PMS5003 sensor is sensitive to the presence of other carbonyl compounds in the sample with a structure similar to formaldehyde (e.g. acetaldehyde and acetone). Moreover, GC-ECD analysis showed low accuracy of the PMS5003 sensor towards formaldehyde. For this reason, this type of sensor may be recommended for determining the total organic compounds (TVOC), but not for the specific identification of a chemical compound such as formaldehyde.

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