Portable and remote electrochemical sensing system for detection of tricresyl phosphate in gas phase

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ABSTRACT

A portable electrochemical sensor has been developed for determination of tricresyl phosphate (TCP) in gas phase. An alkaline catalyst column was used in an automatic TCP sampling system where gasified TCP was hydrolysed to cresol, making it electrochemically detectable. Hydrolysates were then detected in the flow injection analysis (FIA). Amperometric measurements were performed utilizing the unicell, which includes a glassy carbon working electrode, a silver/silver chloride (Ag/AgCl) reference electrode and a stainless steel auxiliary electrode. The response of the system was linear in the TCP concentration range of 5–300 ppb in the gas phase. Commercial jet engine oils containing small amounts of TCP were also analyzed and resulted in signals similar to those from the TCP test and calibration samples.

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1. Introduction

Recently, there is increasing concern regarding some highly publicized incidents, in which illness of flight crew members and passengers have been attributed to possible exposure to jet engine oils containing tricresyl phosphate (TCP) entering the cabin air through the aircraft bleed air systems [1]. Tricresyl phosphate is heavily used in many industrial applications, such as fluid additives, plasticizers, and flame retardants. The US Air Force has employed hydraulic fluids containing organophosphates since the 1970s in its high-performance aircraft [2]. Over the past 30 years, 3% tricresyl phosphate has been added into some commercial jet oils, such as Mobil Jet Oil [3]. Although some amount is decomposed during use [4], the remaining TCP could be released into the cabin air environment during oil leakage on aircraft hydraulic systems [5]. Exposure to passengers occurs mainly through ingestion, inhalation of aerosols, and dermal sorption. TCP is an ester of phosphoric acid and cresols, and any isomeric cresol (o-cresol, p-cresol or m-cresol) can form a TCP molecule. Because of its neurotoxicity, the ortho-isomer of TCP (o-TCP) is intentionally excluded from these fluids [6]. Being a highly toxic compound, tricresyl phosphate inhibits vital enzymes, such as acetylcholine esterase [7], and carboxyesterases [8], as well as inducing an organophosphorous-induced delayed neuropathy (OPIDN) [9–11].

Determination of TCP can be divided into two different groups of methods, mostly distinguished by whether or not the TCP chemical structure is destroyed during the analysis. The destruction of TCP by basic hydrolysis results in the appearance of cresols and phosphates. In general Scheme 1 (see below) is demonstrated the hydrolysis of TCP:

\[ \text{OP(OC}_6\text{H}_4\text{CH}_3)_3 + 3\text{NaOH} \rightarrow \text{Na}_3\text{PO}_4 + 3\text{HOC}_6\text{H}_4\text{CH}_3 \] (1)

The hydrolysis yields three molecules of cresols and a molecule of phosphate ions from one molecule of TCP, and after the hydrolysis completes, either product can be determined. TCP can also be detected without any preliminary modification by chromatographic methods. The most commonly used methods for the detection of TCP include highly sensitive gas chromatography (GC) with a nitrogen– phosphorus sensitive detector (GC/NPD) [12], a flame photometric detector (GC/FPD) [12] or mass spectrometric (MS) recognition [13], high-performance liquid chromatography (HPLC) [14] and thin-layer chromatography (TLC) [15]. However, those systems are expensive, too bulky to be used on-site for continuous monitoring, and need highly trained personnel. Thus, a sensitive, easy to use, and rapid sensing system for TCP detection and monitoring might be useful in a large number of applications. Electrochemical detection can avoid the mentioned drawbacks for chemical analyses and offers considerable promise for micro-fabricated systems with features that include high sensitivity, easy to miniaturize, and low price.

Recently we reported a sensing system for TCP electrochemical detection in air [16]. In this paper we describe the development of a portable and remote electrochemical sensing system for TCP.
determination in gas phase with a new automatic TCP sampling system, optimized elution buffer, and using wireless Bluetooth® technology for device communication. Since TCP itself is electrochemically inactive, an alkaline catalyst was used to obtain hydrolysates that are electrochemically active, i.e. cresol and phosphate ions. TCP was detected in several commercial jet oils and the ability to distinguish between oils containing different concentrations of TCP was demonstrated.

2. Materials and methods

2.1. Reagents and solutions

TCP samples were converted by alkaline hydrolysis to cresol which allows application of electrochemical detection techniques. Alkaline powder was made from NaOH (Fisher, NJ) and neutral alumina oxide (Al2O3) (Sigma–Aldrich, MO). Pipet filter tips (USA Scientific, Inc.) 50 μL beveled filter tips were used to pack alkaline powder. p-Cresol (Acros Organics, NJ) was dissolved in 0.2 M Na2HPO4/0.2 M KH2PO4 buffer (pH = 6.67, NaCl = 10 mM). Na2HPO4 and KH2PO4 were obtained from Fisher, NJ. DI water was used for Millipore Direct-Q water purification system (resistivity 18 MΩ cm). TCP methanol solution and engine oil samples (BP Turbo Oil 274, BP Turbo Oil 2380, and Mobile Jet Oil II) were gasified and hydrolysed in an automatic TCP sampling box.

2.2. Electrodes and portable sensor

All amperometric experiments were performed with CH Instruments (CH1910B) Bi-Potentiostat and duplicated with a handheld potentiostat (Palm-Sens). A desktop computer and pocket PC were used to collect the respective data. The handheld potentiostat communicates wirelessly with the Pocket PC via Bluetooth® (Fig. 1, right). Flow injection analysis (FIA) was carried out using cell electrodes, one of which includes glassy carbon working electrode (2 mm Ø), and another of which includes stainless steel auxiliary electrode and Ag/AgCl reference electrode (BASI, IN) (Fig. 1, left). A coating solution was applied for the Ag/AgCl reference electrode before detection as per instruction from the company. The working electrode was polished with alumina powder (1, 0.3, and 0.05 μm in order). 10 mM NaCl was used to maintain the potential of reference electrode. 0.64 V corresponding to cresol oxidation potential was applied in amperometry. A switch injection unit (Valco Instruments Co. Inc.) was used with a 50 μL sample loading loop. The flow rate was maintained at 200 μL/min by using a single syringe pump (KD Scientific, MA).

2.3. Alkaline catalyst for TCP hydrolysis

Alkaline powder catalyst was prepared by mixing NaOH and Al2O3 (1:10 wt) in ethanol on an automatic stirrer for 1 h until all NaOH was dissolved. The mixture was dried in a vacuum chamber. The dried powder was heated at 100 °C for 5 min in an oven before use. 100 mg of powder was packed into a pipette tip with filter which constituted the hydrolysing column. The conversion of TCP to cresol in alkaline medium is shown in Scheme 1.

2.4. Automatic sampling system for hydrolysis of TCP and engine oils

Since TCP samples in a gas phase are not readily available, it was necessary to prepare such samples for the system calibration. The stock TCP solution (2 mmol/L) was prepared in methanol and diluted to obtain TCP samples with concentrations of interest. Different concentrations of TCP (0, 5, 10, 20, 50, 100, 200, and 300 μM) in 0.5 mL of methanol were prepared and evaporated for 10 min N2 bubbling (during latter 5 min an elevated temperature of 230 °C was used to make sure all TCP was evaporated). N2 flow rate was maintained at 1.1 L/min, which made the total air volume equal to 11 L (11 L/22.4 L = 0.5 mol). Therefore, the concentrations of 0, 5, 10, 20, 50, 100, 200 and 300 ppb in air of TCP were realized. All gas TCP samples were blown through alkaline powder catalyst column, and then 3 mL of Na2HPO4/KH2PO4 (0.2 M/0.2 M final concentrations) and 10 mM NaCl buffer was flushed through the column to collect the hydrolysed products. 10 mM NaCl was added into the buffer to maintain constant potential of reference electrode. All steps above from gas sample collection to buffer flushing were done with the automatic TCP sampling system built in our lab (Scheme 2). By this processes, TCP gas samples were converted to liquid samples containing corresponding concentrations of cresol, making it possible to detect TCP by an electrochemical method.
Engine oil samples were prepared by dissolving the samples into methanol in 2 µL/0.5 mL ratio and with the same processes as TCP samples. Oil BP274 does not include TCP, Mobile Jet Oil II includes 1–3%, and BP2380 includes 1–5% TCP [17]. BP274 oil spiking with TCP with different concentrations were also prepared, sampled, and measured.

3. Results and discussion

3.1. Performance of the electrochemical sensor

The performance of the three-electrode glassy carbon system was examined by flow-injection of cresols with differing concentrations. During the oxidation of cresol, electrons were released and transferred to the working electrode. The same amount of electrons was compensated at the auxiliary (or, counter) electrode [18]. The total number of electrons transferred at the electrode in a unit time must be proportional to the quantity of cresol reaching the electrode in that time period. Moreover, no electro-migration occurred because cresol is neutral in charge, which makes the process simply diffusion controlled. The rate of diffusion mass transfer is proportional to the concentration gradient at the electrode surface. Because the applied potential was constant in amperometric mode, the ratio between oxidized and reduced products was constant as well, ensuring that the current was proportional to the concentration of injected cresol [18].
The calibration curve for cresol injections is shown in Fig. 2. Five different concentrations of cresol were injected into the measurement cell, as shown in the inset figure. The current peak increases linearly with the concentration of cresol (250–3000 nM). The sensitivity is 0.025 nA/nM, which is referred to glassy carbon electrode with diameter size 2 mm. The $R^2$ coefficient of determination, 0.992, shows the goodness of linear fit in such a concentration range. The detection limit of less than 250 nM can be estimated from the signal-to-noise ratio ($S/N = 3$), while the previously reported detection limit was 600 nM [16]. The decrease in response with subsequent injection of high concentration of cresol is due to the fouling of electrode from cresol oxidation [16].

![Fig. 2. Calibration curve of cresol detection. The inserted figure shows the amperometry for cresol detection. Note that the baseline was subtracted. The decrease in response with subsequent injection is due to the fouling of electrode from cresol oxidation [16] (seen on the inset figure). $R^2$, coefficient of determination, representing the goodness of linear fit, in calibration curve is 0.992. Data points in calibration curve correspond to the average of the three injections. Error bars are the standard deviation of triple experimental results. Detection limit is 250 nM.](image)

To show the ability of this system for TCP detection in gas, TCP with concentrations of 0, 5, 10, 20, 50, 100, 200, 300 ppb were sampled and measured. The data obtained in the flow injected system are shown in Fig. 3. For each set of amperometric measurement, several TCP concentrations were injection in random order, one example of which is shown in the inset of Fig. 3. This procedure was repeated six times. The equation of linear fit is $y (nA) = 1.22x$ (ppb) + 36.5. The $R^2$ coefficient of determination, 0.990, shows the goodness of linear fit in such a concentration range.

3.2. Detection of hydrolysates from TCP samples

![Fig. 3. Calibration curve of TCP hydrolysate samples. Linear concentration ranges from 5 ppb to 300 ppb in gas. The inset figure shows one set of raw amperometric results out of six times measurements. The linear fit for the inset figure is $y = 1.22x + 36.5$, and the $R^2$ is 0.99. The results show the ability of this sensing system to detect TCP in a wide concentration range. The conversion of concentration units between ppb in gas and μM is as below. TCP was dissolved in 0.5 mL of methanol, which would be vaporized and dispersed in 11 L of N₂. Approximately, 11 L of gas is 0.5 mol. Therefore, 1 μM of TCP in methanol solution corresponds to 1 ppb in gas.](image)

To test the ability of this system to determine TCP in air from real samples, such as samples from jet engine oils, 2 μL of commercially available BP Turbo Oil 274, BP Turbo Oil 2380, and Mobile Jet Oil II were mixed in 0.5 mL of methanol and were used to prepare the hydrolysate samples with the same processes as TCP hydrolysates described above. The data of oil hydrolysates are shown in Fig. 4. For

![Fig. 4. Amperometric results of injections of different oil hydrolysate samples inset with one example of raw data. They were prepared, gasified, and hydrolysed in the automatic sampling system before detection. Note that fouling contributes to the existence of error bar and the concentrations of TCP in these oil samples are much higher than what would be expected in an aircraft cabin. All samples were measured randomly for three times.](image)

3.3. Detection of hydrolysates from engine oils

![Fig. 5. Amperometric results of injections of oil spiking TCP hydrolysate samples. The slope of linear fit is around 1 nA/ppb, which is close to Fig. 3. $R^2$ of 0.99 represents the goodness of linear fit. All samples were measured randomly for three times.](image)
each set of amperometric measurement, several oil samples were injected in random order, one example of which is shown in the inset of Fig. 3. This procedure was repeated three times.

Fig. 5 shows results of measurements in BP274 oil spiked with TCP in 0, 50, 100, and 200 ppb concentrations. The slope of linear fit is around 1 nA/ppb which is close to that in Section 3.2.

Concentrations of TCP in these oils are summarized in Table 1. Using the linear fit in Section 3.2 (Detection of hydrolysates from TCP samples), we calculated the concentration of TCP from peak current. And the conversion from ppb unit to % unit was done similarly as previously described in Section 3.2. The electrochemical responses from the oil hydrolysates had a similar trend compared to the TCP concentrations in the oils as expected from manufacturers’ data. Thus, the system appears to be capable of detecting TCP in oils and may have application in aircraft and other transportation vehicles.

4. Conclusions

In summary, a portable and remote electrochemical sensing system has been developed for the fast determination of tricresyl phosphate (TCP) in gas phase. The TCP gas sample was produced from both TCP methanol samples and commercial jet engine oils. TCP was hydrolysed by alkaline catalyst to cresol which makes electrochemical detection possible. An automatic TCP sampling system built in our lab was successfully used to convert TCP to hydrolysate buffer solution, which was detected in a portable sensing system. A remote sensor was realized by the usage of Bluetooth® between a pocket PC and a potentiostat. We have demonstrated that a detection limit for TCP down to 5 ppb in gas is possible. The response to commercial jet engine oils is similar to that of TCP methanol samples. The advantages of this system, such as easy operation, remote analysis, quick response, and low cost, make on site monitoring of aircraft cabin air, as well as other air environments, potentially practical. The future investigation should focus on the design of an automatic sensing system, as well as reducing fouling on the electrodes.

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References


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