SPECIFICITY USING ELECTROCHEMICAL FUEL CELL SENSORS IN SCREENING AND EVIDENTIAL BREATH TESTING

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SYNOPSIS

The specificity of current breath alcohol instruments to possible interfering substances is briefly reviewed. Instruments based on an electrochemical fuel cell sensor already have inherent specificity to substances such as acetone and hydrocarbons. The specificity of the fuel cell sensor can be further enhanced by detailed analysis of the signal output.

We present the analysis of ethanol solution containing trace methanol.

INTRODUCTION

In recent years there has been increasing emphasis in many countries on the use of breath alcohol levels as a measure of driving impairment. The majority of countries with drink-driving legislation have invariably used breath measurement for screening purposes, but only countries such as the United States, Canada, Australia, Japan, Portugal, Northern Ireland and more recently, Great Britain (UK Transport Act, 1981) have adopted legislation which allows breath alcohol levels to be used as a basis for conviction, instead of blood or urine.

With the increased use of evidential breath instruments to replace blood or urine alcohol analysis, it is therefore important that the breath alcohol readings presented to court are as unequivocal as those obtained from blood alcohol analysis using gas chromatography or the ADH enzymatic method. With the wide variety of breath alcohol instruments

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now available, it is generally accepted that the majority of instruments, whether based on colorimetry, infra-red, or electrochemical principles, are more than adequate for measuring ethyl alcohol when it is the only volatile constituent present in breath. There are numerous correlation studies which testify to this (e.g., Emerson et al., 1980; Isaacs et al., 1983).

One of the main challenges to the acceptance of breath in the courts is usually based on the specificity of a particular method, with defense experts claiming that the client's reading is due to acetone, methane, petrol, solvents, or constituents of various diets. Although it can invariably be proved that the presence of such substances, whether consumed or inhaled, would be insignificant even if they interfered, nevertheless it is very much more conclusive if the presence of interfering substances is demonstrated.

SPECIFICITY OF EVIDENTIAL INSTRUMENTS IN CURRENT USE

Infra-Red Detectors

Infra-red detectors based on absorption of ethyl alcohol at a selected wavelength have generally limited specificity but, by the use of multiple filter arrangements or by using a secondary sensor such as a semi-conductor (Hutson & Forrester, 1981), the specificity can be improved although not to the extent that it can distinguish between different alcohols or aldehydes, or between ethanol and certain hydrocarbons.

Gas Chromatographic Analyzers

Although breath alcohol instruments have been developed based on gas chromatography (Penton & Forrester, 1969), the technique is not widely used, mainly because with the accompanying gas cylinders it is not the ideal method for routine use by police officers.

Fuel Cell Sensors

Instruments based on an electrochemical sensor (Jones & Williams, 1972) which only respond to volatile substances that can be electrochemically reduced or oxidised at a platinum electrode surface have, therefore, some inherent specificity, in that they are not sensitive to breath acetone or solvents based on derivatives of organic hydrocarbons. These substances are often encountered in industrial working environments. The fuel cell sensor will, however, also respond to other aliphatic alcohols and
aldehydes if they are present, although in practice these are very seldom encountered in breath in significant concentrations. On these occasions, however, it is not necessary to analyze quantitatively the substances which may be interfering but only to indicate their presence.

This paper describes how by a detailed analysis of the fuel cell response the Auto Alcolmeter Instrument can be used to give improved specificity compared with infra-red instruments in current use.

FUEL CELL INSTRUMENT WITH IMPROVED SPECIFICITY

Auto Alcolmeter

This instrument utilizes a fuel sensor and is shown schematically in Figure 1. A 1.5-cc sample of end-expired breath is electrochemically oxidized at a specially prepared platinum electrode surface generating a signal that is a function of the alcohol concentration. The principle is now well established and forms the basis of the range of Alcolmeters manufactured by Lion Laboratories Limited, now in worldwide use for both screening and evidential purposes.

The Auto-Alcometer is microprocessor-controlled and enables a complete breath test to be conducted with minimum operator involvement. This includes calibration either on a dry gas standard or a wet breath simulator. The result of the test (i.e. the maximum output of the fuel cell) is displayed and recorded on a print out.

Fuel Cell Response Analysis

The output voltage of a fuel cell of this type as a result of receiving a sample of oxidisable gas has been examined (Huck, 1969). Examples of the response of a typical cell to individual samples of ethyl and methyl alcohols are shown in Figure 2. The equation that has been proposed is:

\[ v(t) = \frac{V_0}{k_2 - 1} \left[ \exp(-k_1 t) - \exp(-k_2 t) \right] \]  

(1)

where \( k_1 \) = reaction rate at the electrode (per second) 
\( k_2 \) = discharge rate of the cell (per second) 
\( V_0 \) = maximum voltage achieved on open circuit
The determination of $k_1$ and $k_2$ by numerical analysis routines can be difficult and iterative procedures can prove to be unstable in functions of this form. However, we are not primarily interested in the amplitude and so if we apply the transformation

$$z(t) = \frac{v(2t)}{v(t)}$$  \hspace{1cm} (2)$$

we obtain

$$z(t) = \exp(-k_1t) = \exp(-k_2)$$  \hspace{1cm} (3)$$

This function poses a relatively simple task for analysis. Examining the function at 3 time values, $t$, $2t$ and $4t$, yields $z(t)$ and $z(t)$ and $z(2t)$; hence

$$k_1 = \frac{1}{t} \log \left[ \frac{1}{2} \left( \sqrt{2z(2t) - z^2(t)} \right) \right]$$  \hspace{1cm} (4)$$

The response of several fuel cells to samples of ethyl alcohol and for other alcohols, including methyl, butan-1-01, and propan-1-01, was examined. The errors in the values of $k_1$ obtained for these alcohols showed a trend suggesting a deviation from Equation (4) to include higher orders of $k_1$. This investigation is continuing. However, values of $z(t)$ with the range of alcohols studied showed excellent discrimination for values of $t$ in a particular time range. This was the basis of a technique to show the presence of trace contaminants in a sample of ethyl alcohol.

A program was developed for the Auto Alcometer to analyze the fuel cell response to samples of ethyl alcohol with and without the presence of contaminants, such as other alcohols or aldehydes. The instrument is first calibrated with an 80 mg% ethyl alcohol standard. Two samples are then taken and analyzed followed by a second calibration with the same 80 mg% ethyl alcohol standard. A statistical examination of the $z$ values obtained is provided to show the presence of a contaminant at a 95% confidence level. The print out shown in Figure 3 is an example of the result of an analysis of a sample of 80 mg% ethyl alcohol to which a 10 mg% amount of methyl alcohol had been added.
CONCLUSION

The above method shows that by analysis of the signal response, the inherent specificity of the fuel can be further enhanced and, in so doing, assist to provide the courts with unequivocal evidence of ethanol levels unaffected by other possible breath volatiles. In the rare event of the presence of other breath volatiles, which interfere with fuel cell response, the print out shows "TRACE DETECTED" and enables the officer to refer the subject to blood or urine analysis.

REFERENCES


Figure 1. AUTO ALCOMETER operating principles.
Figure 2. Fuel cell response for ethanol and methanol.

Figure 3. AUTO ALCOLOMETER print-out for sample containing trace methanol.