Fluoride Selective Electrode Procedure for Fluorated Organophosphate Cholinesterase Inhibitors

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Abstract. Manual and automatic determinations of Sarin with a fluoride selective electrode after alkaline hydrolysis are presented. Comparison with a classic colorimetric method shows excellent agreement between the two methods.

Enzymatic hydrolysis (acetylcholinesterase) measured with an enzyme-electrode, yields no results: the assumption that Sarin loses F\(^-\) upon reaction with cholinesterase is proved to be incorrect.

Key words: Fluoride Selective Electrode — Sarin — Alkaline Hydrolysis — Enzymatic Hydrolysis.


Die enzymatische Hydrolyse (Acetylcholinesterase) unter Anwendung einer Enzymelektrode, gibt keine Resultate: die Annahme, daß Sarin bei der Reaktion mit Cholinesterase F\(^-\) verliert, ist nicht richtig.


Introduction

Cholinesterase inhibitors of the organophosphate type, such as Sarin, are usually determined by gas liquid chromatography or by indirect spectrophotometry based on enzymatic hydrolysis of an appropriate substrate. One of the products resulting from the hydrolysis is made to react with a reagent, thereby forming a coloured compound.

The use of an acetylcholine selective electrode was reported by Baum and Ward (1971), and more recently von Storp and Guilbault (1972) used a sulphide ion selective electrode for the measurement of the thiocholine liberated by hydrolysis of acetylthiocholine.

In this article the use of fluoride selective electrode for the measurement of Sarin is reported.
Experimental

Colorimetry: a manual version of the automated indirect colorimetric method of Voss (1969) was used.

Potentiometry:

Apparatus: Radiometer 26 pH-meter, Orion Fluoride Electrode 94-09-00, Standard Calomel Electrode.


Manual Procedure

Add 3 ml of 3 M NaOH to 50 ml Sarin solution in a 100-ml thermostated (± 25 °C) plastic vessel. Mix and agitate for 15 min. Add 2 ml concentrated acetic acid (18 M), mix and add 20 ml TISAB solution containing 90 p.p.b. fluoride ion (to increase the sensitivity — see results and discussion). The electrodes are immersed in the solution stirred at a moderate speed. Record the potential after 10 min. Prepare a blank in the same way but use 50 ml H2O instead of the Sarin solution. All measurements are carried out in thermostated plastic vessels. The concentration of fluorides obtained from the calibration curve is multiplied by 7.83 to obtain the Sarin concentration.

Automatic Procedure

The automatic system is shown in Fig. 1. A technicon Autoanalyzer sampler II (sampling rate 10 or 20 samples per hour, sample-to-wash ratio 1:1) and a proportioning pump I were used.

The electrodes were mounted in perspex (methylmethacrylate) flow-through cells designed at the laboratory. The indicator electrode cell volume was about 50 μl. The electrodes were connected to a two-pen recorder via the pH meter and a baseline adjustment unit, which was also designed at the laboratory.

It is necessary to know exactly what quantity of fluoride ion is added via the TISAB solution (see Fig. 1). Therefore, it was determined by a blank run against a calibration line. This is necessary because flow-rates in the automatic system can deviate from the value given by the manufacturer with as much as 10%, thereby causing the same error in the mixture entering in the flow-through cell.

Choice of pH

The rate of hydrolysis of Sarin at different pH-levels was determined by means of an automatic two-channel system. The sample was pumped through one channel and the TISAB solution containing 100 p.p.b. F⁻ ion through the other. After mixing in a single mixing coil, since the flow ratio was 1:1, the solution contained 50 p.p.b. added F⁻. This addition is necessary to increase the sensitivity, as is explained under results and discussion.

The first 50 ml of the sample consisted of a buffer solution, which was pumped through the measuring cell to obtain a steady baseline. Then 1 ml Sarin solution was added to the sample and the hydrolysis was followed continuously. Below pH 5 to 6 practically no hydrolysis occurred, while at pH 11.5 it was complete after 10 min.