

## CONCLUSIONS

Hydrolysis reaction inside flow system avoids sample handling and control of hydrolysis time unlike other methods published (6). Furthermore, the use of oxidative detection mode avoids the need to remove dissolved oxygen.

With the proposed method it is possible to determine Paraoxon in the presence of Parathion, with an error lower than 5% for Parathion/Paraoxon ratios below two.

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## DEVELOPMENT OF FLOW INJECTION AMPEROMETRIC MONITORS FOR THE DETERMINATION OF NITRATE AND OTHER SPECIES

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Our studies of applications of flow injection analysis with amperometric detection suitable for use in monitoring situations have been carried out mainly using a laboratory built wall-jet detector which holds only a glassy carbon working electrode.<sup>1</sup> This is used partly immersed in a suitable electrolyte in conjunction with conventional saturated calomel reference and platinum foil counter electrodes. Phosphate can be determined by injecting samples into a carrier stream of an acidic molybdate reagent.<sup>2</sup> The 12-molybdo-phosphate formed is determined by reduction at the glassy carbon electrode held at +300 mV vs SCE. For determinations in inexpensive and plentiful samples, such as a hydroponic fluid, the reverse flow injection method (rFIA), in which acidic molybdate reagent is injected into a sample stream, can be used more appropriately.<sup>3</sup>

The shapes of signals obtained in rFIA would be expected to be different from those obtained in normal FIA.<sup>4</sup> In nFIA reaction occurs initially at the two extremities of the sample bolus but after

relatively little dispersion an excess of reagent reaches the centre of the bolus and a conventionally shaped single peak is obtained. In rFIA the sample concentration at the centre of the reagent bolus is initially zero. With increasing dispersion, however, the equivalent sample concentration increases throughout the reagent bolus to the limiting concentration in the sample stream. The shapes of these peaks have been discussed elsewhere.<sup>4-6</sup> The advantages of using rFIA are that reagents are conserved, the sample is determined with minimal dilution, and determinations of several species can be made on the same sample stream using different chemistries.<sup>2</sup> rFIA signals are more prone to the formation of double peaks and it is usually necessary to use small injection volumes in order to obtain "single" peaks.<sup>6</sup>

Another on-line reaction which has proved useful in monitoring situations involves injection of nitrite into an acidic bromide carrier stream:<sup>7</sup> the nitrosyl bromide formed is determined reductively at a glassy carbon electrode held at +200 mV vs SCE.

Several chemistries have been developed for on-line use in which a monitorand is produced in the rFIA manner and part of this is consumed by a determinand dispersing in the nFIA manner.<sup>5,8,9</sup> Thus if acid is injected into a slightly alkaline carrier stream containing nitrite and excess of bromide, nitrosyl bromide is formed in the reverse FIA manner. If an acidic solution of an aromatic amine is injected instead some of the nitrosyl bromide is consumed in diazotising the amine and a reduced signal is obtained, the reduction in size being proportional to the amine concentration.<sup>8</sup> Similarly on-line brominations (and oxidations by bromine) can be used to determine

e.g. amines and phenols, the carrier stream in this case being a slightly alkaline solution of bromate and excess of bromide.<sup>9</sup> Iodine can be formed on-line from iodate, iodide and acid and used to determine e.g. sulphite and ascorbic acid.<sup>5</sup> Signals obtained for the rFIA formation of iodine and the determination of sulphite indicate the characteristics of rFIA signals: at low flow rates the double-peaked nature of the iodine signal is apparent and this is emphasised in the presence of sulphite.<sup>5</sup>

Work is now in progress in adapting the above on-line chemical reactions for application in the capillary fill device (CFD) - a form of disposable sensor - patented by Unilever Research. The device consists of two plates fixed perhaps 100  $\mu$ m apart. On one plate carbon and silver electrodes, and on the other plate chemicals, are screen printed. Sample solution is taken up by capillary action, the chemicals above the electrodes dissolve and a current signal is obtained. We have shown that preformed 12-molybdophosphate gives the expected response in the CFD, and we are now studying the screen printing of phosphate and acidic chemicals to test the device fully for this chemistry. The chemistries for determining nitrite, amines, phenols and sulphite will also be tested.

Our recent work in developing a FIA amperometric monitor for detecting nitrate coincided with the beginning of our interest in the CFD device as will be seen from the following description of our work in this area. Nitrate is frequently determined after reduction to nitrite, but this reduction step can cause problems. Our initial aim was to produce an amperometric monitor based on nitration of an organic compound that would nitrate easily in the least concentrated

sulphuric acid and to a nitro derivative that would reduce on a glassy carbon electrode at a potential more positive than about -300 mV vs SCE, at which potential there would be no interference from dissolved oxygen; demanding requirements! Of some 15 compounds chosen for study polarographically in a screening test benzoic acid proved to be the most suitable reagent. The polarographic method of determining nitrate which was developed is simple:<sup>10</sup> 1 ml of nitrate sample solution is vortex mixed with 3 ml of a  $10^{-2}$ M solution of benzoic acid in concentrated sulphuric acid for 30s and the resulting mixture is diluted to 25 ml with water and polarographed. A reduction peak is obtained at -130 mV due to complete formation of 3-nitrobenzoic acid: nitrate can be determined readily by differential pulse polarography in the sample range  $1 \times 10^{-5}$  M to  $5 \times 10^{-3}$  M.

Unfortunately benzoic acid was found to be nitrated insufficiently rapidly for use in an on-line reaction: further the single LSV peak of 3-nitrobenzoic acid on a glassy carbon electrode occurs at -450 mV vs SCE. Thiophene-2-carboxylic acid proved to be the most suitable reagent for on-line use being nitrated extremely rapidly. Two LSV peaks are obtained on a glassy carbon electrode at -190 and -390 mV. The first peak is due to reduction of the 5-nitro derivative (reported to be formed in 41% yield) and the second peak to reduction of the 4-nitro derivative (55% yield). Reduction of dissolved molecular oxygen interferes only slightly with the first wave. A flow injection method was developed in which the nitro derivatives were formed in the rFIA manner.<sup>11</sup> Thiophene-2-carboxylic acid (25  $\mu$ l,  $10^{-1}$ M in concentrated sulphuric acid) was injected into the nitrate sample solution which had been made 1.5M in sulphuric acid. 5-Nitrothiophene-2-carboxylic acid was monitored at a glassy

carbon electrode held at -300 mV: the transmission tubing was 4.2 mm long with 0.58 mm internal diameter. Nitrate was monitored in the range  $1 \times 10^{-4}$  to  $5 \times 10^{-3}$  M. Contamination of the electrode was apparent after about 15 injections causing a 10% loss of signal.

Chloride is known to be a possible interferent in nitration reactions and use was made of this in developing an even simpler and more satisfactory method<sup>12</sup> In this method 25  $\mu$ l of concentrated sulphuric acid was injected into the nitrate sample solution which had been made 2M in hydrochloric acid. The signal at a platinum electrode (a Dionex cell was used) held at +700 mV vs Ag/AgCl due to reduction of the nitrosyl chloride and chlorine formed was monitored. The use of a 40 cm long single bead string reactor as transmission tubing delayed dilution of the sulphuric acid and enhanced the signal. The signal to noise ratio is greater when a monitoring potential of 700 mV is used rather than 300 mV at which latter potential a slightly higher signal is obtained: further, at 700 mV iron(III) and copper(II) are not reduced and do not interfere. No electrode contamination problems were observed with this system.

Clearly these two flow injection methods suffer from the need to inject concentrated sulphuric acid into the sample carrier stream. For application in a monitoring device use of the pecking sampling device of Riley et al<sup>13</sup> might be used with advantage; we hope to investigate this shortly.

At this stage attention was turned to the use of the capillary fill device. Previous studies by others had shown that nitrate could be reduced effectively on a copper electrode but only if the copper

surface was freshly formed.<sup>14</sup> We have used the CFD with nitrate solutions made 1M sulphuric acid,  $5 \times 10^{-3}$  M in copper sulphate and  $2 \times 10^{-4}$  M in sodium chloride. When the screen printed carbon electrode is held at -700 mV vs the internal reference electrode copper is plated onto it and oxygen in the solution is reduced. The nitrate can then be determined at -880 mV by scanning to more negative potentials.<sup>12</sup> Studies now need to be made of the screen printing of the reagents involved onto the upper plate of the device.

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