CHAPTER 4

CONCLUSIONS

Flow injection procedures for the determination of anionic surfactants, hyoscine butylbromide, yttrium, cobalt and manganese have been developed.

FIA for Anionic Surfactants

The preliminary study of a FIA method with on-line single solvent extraction for the determination of anionic surfactants was investigated. The method is based on an ion-pair extraction reaction with methylene blue in chloroform. The anionic surfactant reacts with MB to form an ion associate, which can be extracted into chloroform. A standard or sample was injected into a stream of MB solution before being segmented with chloroform at a segmentor. The coloured ion association compound was extracted into chloroform when the segments moved along an extraction coil. The chloroform phase was separated from the aqueous phase by using a PTFE membrane phase separator. The absorbance of the chloroform stream was continuously monitored at 650 nm. Optimization was carried out and the optimum conditions are summarized in Table 3.8. The smooth base line could be achieved when the water-equilibrated chloroform was used. A calibration was a plot of peak height against concentration (0.025-0.10 mg SDS/l). A detection limit ($3S_B$) of 0.04 mg SDS/l, RSD of 3.8% (for 0.10 mg SDS/l; $n = 9$) and average percentage recovery of 100% (for natural water) were obtained. The proteinaceous material present in waste water samples could interfere the determination of anionic surfactants. This preliminary study with on-line single solvent extraction was useful for the first designation of a FIA manifold with on-line double solvent extraction.

S. Fan and Z. Fang [63] reported an FIA system with two-step solvent extraction for the determination of anionic surfactants and used T-design gravity phase separators. However, when using this gravitational phase separator considerable care and experience are required to avoid contamination of the flow-cell with aqueous phase particularly at the beginning of the operation. In this work, the FIA procedure involving on-line double solvent extraction using membrane phase separators for the determination of anionic surfactants in waters was investigated. Using the PTFE membrane phase separators overcome the contamination of the flow-cell with aqueous phase. The method is based on the Abbott's batch method (modified from Longwell and Maniece procedure). The methylene blue-anionic surfactant ion associate is partitioned into chloroform from an alkaline MB solution and then back-extracted with an acidified MB solution to avoid the negative interference of proteinaceous material present in environmental samples and in order to remove the interference of those materials such as inorganic anions e.g. nitrate, chloride etc. that form MB complexes of low chloroform extractability respectively. A standard or sample was injected into the stream of alkaline MB solution and then merged with a chloroform stream to create segments by a segmentor. The extraction took place during the segments passing the extraction coil, until reaching a PTFE membrane phase separator where the chloroform phase was separated out and flowing further to merge with the stream of acid MB at another segmentor. Back-extraction took place during the passage through the second extraction coil. The second PTFE membrane phase separator separated the chloroform phase out and the absorbance of the chloroform stream was continuously detected at 650 nm. Optimum conditions are shown in Table 3.17. The water-equilibrated chloroform resulted a smooth base line and higher peak height comparing to the results obtained when using the chloroform without water-pre-equilibration. A calibration graph was a plot of peak height against concentration (0.02-0.40 mg SDS/l). A detection limit ($3S_B$) of 0.02 mg SDS/l and precision of 1.3% RSD (for 0.40 mg SDS/l; n = 21) were obtained. A throughput of 30 injections/h could be achieved. This was 2 min per an analysis when comparing to 24 min of a batch procedure. This minimizes reagent consumption, especially chloroform that is toxic waste. The chloroform waste could also be recycled for reuse by distillation. The following species: urea, NH_4^+, NO_3^-, S_2^-, Cl^- and SO_4^{2-} did not interfere in the determination of SDS (0.10 mg/l) when the concentrations did not exceed 1000, 100, 100, 100, 1000 and 500 mg/l respectively. The application of the proposed procedure to determination of anionic surfactants in different types of water, the results obtained by the FIA method agreed with the batch ones (Abbott's method). The recoveries were found to be 100±10% and 100±20% for the FIA and batch procedures respectively. Sample pretreatment using centrifugation should be used.

FIA for Hyoscine Butylbromide

The British Pharmacopoeia [77] reported the extractive spectrophotometry using hexanitrodiphenylamine as ion-pair reagent for the determination of hyoscine butylbromide (HB). Hexanitrodiphenylamine is an explosive chemical, so it is dangerous and difficult to use. In this work, the FIA system involving on-line solvent extraction for the determination of HB was developed. The method is based on the extraction of ion association compound formed between HB and bromothymol blue (BB) into chloroform. The extraction of ion association compound into chloroform and measurement of the yellow colour in separated chloroform phase were continuously done. A standard or sample was injected into a carrier stream of borate buffer (pH 10.0) solution and then merged with the chloroform stream at a segmentor to create segments. The extraction took place during the segments passing an extraction coil. The chloroform phase was separated from the aqueous phase by using a PTFE membrane phase separator, and the absorbance of the separated chloroform stream was continuously monitored at 420 nm. Optimum conditions are summarized in Table 3.45. A smooth base line and higher peak height were obtained when water-equilibrated chloroform was used. A calibration graph was linear up to 200 mg HB/l, with a detection limit ($3S_B$) of 18 mg HB/l. RSD of 1.2% (for 120 mg HB/l; n = 11) was obtained. Lactose up to 4000 mg/l did not interfere the determination of HB (100 mg/l). The developed FIA procedure was applied to determine the hyoscine butylbromide contents in 10 mg HB tablets. The percentage recoveries were found in range 80-100%.

FIA for Yttrium

The ICP-AES was used as routine method for the determination of yttrium in ore leachates samples. This method is difficult and consumes high cost. In this work, a simple flow-injection spectrophotometric procedure for the determination of yttrium using arsenazoIII was investigated. The method is based on the complex formation between yttrium(III) and arsenazoIII at pH 4.0. The preliminary studies, spectral characteristics of yttrium-arsenazoIII complex, were done using batch procedure. The most appropriate pH range for colour formation was pH 2.3-5.5, with an acetic acid/acetate or KHP/HCl buffer. The batch arsenazoIII method was adapted to a simple FIA procedure. A standard or sample was injected into a carrier stream of acetic acid/acetate buffer (pH 4.0), which passed through a mixing coil before merging with the reagent stream of arsenazoIII. After passing through the second mixing coil, the coloured complex was continuously monitored at 650 nm. Optimization was done and the optimum conditions are shown in Table 3.63. The KHP/HCl buffer (pH 4.0) could be used instead of acetic acid/acetate buffer (pH 4.0), while citrate buffer (pH 4.0) could not. This is because citrate forms a stable complex with yttrium, which prevents it from reacting with the arsenazoIII reagent. A calibration graph, plotted of peak height against concentration, was linear up to 1.00 mg Y/l with a detection limit ($3S_B$) of 0.02 mg Y/l. Precision of 0.8% RSD (for 0.40 mg Y/l; n = 11) was obtained. A throughput of 60 injections/h can be achieved. Summarized results for the effect of interfering ions are shown in Table 3.67. The proposed FIA procedure was applied to ore leachates of reference materials and samples. Yttrium contents in samples obtained by the proposed FIA procedure agreed with the ones analyzed by ICP-AES.

FIA for Cobalt and Manganese

The routine method used for the determination of Co(II) and Mn(II) in reused catalyst samples was ICP-AES. In order to reduce the operation cost of this method, the simple spectrophotometric FIA procedures for the determination of Co(II) and Mn(II) have been developed.

The stock standard solutions of Co(II) and Mn(II) were prepared in mixed solvent (70: 22: 8 by volume of glacial acetic acid: xylene: deionized water) so the components in these solutions were similar to solvent system of liquid residue samples. 50% (v/v) Isopropanol solution was selected to dilute the samples and stock standard solutions as optimum compatible solvent so the experiments can easily proceed in aqueous system. The spectral characteristics of Co(II)-PAR complex and Mn(II)-formaldoxime complex were preliminary studied. Absorption spectra showed the maximum absorption of Co(II)-PAR complex (pH 6.0) and Mn-formaldoxime complex (pH 10.0) at 510 and 450 nm respectively.

The spectrophotometric FIA procedure for Co(II) is based on formation of Co(II)-PAR complex at pH 6.0 which is continuously monitored at 520 nm and the one for Mn(II) is based on formation of Mn(II)-formaldoxime complex at pH 10.0 which is continuously monitored at 475 nm. Attempts have been made to analyze Co(II) and Mn(II) by the same manifold in order to obtain a rapid, simple and economic method. Optimization was done and the optimum conditions for the determination of Co(II) and Mn(II) are summarized in Table 3.77 and Table 3.89 respectively. For the determination of Co(II), a calibration graph was linear up to 9.0 mg Co/l with a detection limit ($3S_B$) of 0.8 mg Co/l and precision of 0.3% RSD (for 6.0 mg Co/l; n = 11) was obtained. For the determination of Mn(II), a calibration graph was linear up to 9.0 mg Mn/l with a detection limit ($3S_B$) of 0.2 mg Mn/l and precision of 2.3% RSD (for 6.0 mg Mn/l; n = 11) was achieved. Mn(II) and Co(II) up to 12.5 mg/l did not interfere the determination of each other (6.0 mg/l) and Br^- up to 20.0 mg/l did not interfere the determinations of Co(II) and Mn(II). Increasing the ratio of deionized water in stock standard solution up to 20% by volume did not effect the both determinations. The application of the proposed FIA procedures to determine Co(II) and Mn(II) contents in reused catalyst samples were done. The results for Co(II) and Mn(II) contents in reused catalyst samples determined by the developed FIA procedures agreed with the ones analyzed by ICP-AES.