CHAPTER 4

Conclusions

A novel microcolumn system for enhancing performance in flow injection spectrophotometric preconcentration, separation and determination of copper(II) has been developed.

Development of the FIA spectrophotometric procedure for copper(II) determination

The preliminary study on the FI spectrophotometric determination of copper(II) based on a complexation reaction with nitroso-R salt was investigated. Various factors influencing the sensitivity of the method were optimized using the univariate method and the optimum conditions are summarized in Table 3.10. Then the simplex optimization method was used to confirm the optimum conditions, which are obtained by the univariate method. It was found that the optimum conditions by the simplex optimization are similar to those obtained by the univariate method. The calibration curve over the concentration range of 1.0-7.0 mg/l was obtained. The relative standard deviation for determining 4.0 mgCu(II)/l was 0.47% (n=11). The detection limit (3σ) was 0.68 mg/l. This method has been proven to be very sensitive, reproducible and rapid with a sample throughput of 150 h^{-1}. The validity of the method has been satisfactorily examined for the determination of copper(II) in wastewater and copper ore samples. The accuracy was found to be high, because the student t-values were calculated to be less than the theoretical values when the results were compared with those obtained by FAAS.

Development of novel sorbents for the preconcentration of copper(II)

In order to enhance the performance of the preliminary FIA system and apply to trace copper(II), the adsorption efficiencies of copper(II) on Lopburi perlite and synthetic zeolites from perlite were studied. The simple zeolitization of perlites were carried out by treating the perlite with NaOH solution and heating them under reflux at a temperature of 90 °C for 3 hours. Then, the adsorption of copper(II) ions on both the perlites and zeolites formed have been investigated by batch-wise process. The pH values for optimum adsorption of the all sorbents were found to be 5.0 and the optimum temperature range was 22-40 °C. It was indicated that adsorption of copper(II) on both perlites and zeolites could be carried out at room temperature. The rate of copper(II) uptake on natural and expanded perlites were rapid initially and unchanged after 10 min, while both of the synthetic zeolites remain almost unchanged regardless of any change in the shaking time. This is an advantage for wide applications to the treatment of wastewater or trace copper preconcentration by using perlites and the zeolites. In order to model the adsorption behaviors of the sorbents tested the adsorption isotherms were studied. The results obtained show that the adsorption of copper(II) on perlites and the zeolites formed follow both Freundlich as well as Langmuir type adsorption isotherms. However, the Langmuir equation is better obeyed by the system than the Freundlich one as can be seen from the regression coefficient data. The decrease in retention capacity of copper(II) on the sorbents is according to the following sequence: zeolite from expanded perlite > zeolite from natural perlite > expanded perlite > natural perlite (Table 3.32). It was indicated that both zeolites formed should be useful to the preconcentration of copper(II). However, the particle size of the synthetic zeolite from expanded perlite is smaller than 100 mesh size, which is too fine for using in the microcolumn, because the sorbent particles should not be so fine as to create excessive back-pressure under normal sample loading flow rates. So the synthetic zeolite from natural perlite has been proposed as a novel packing material for FIA on-line column preconcentration of copper(II).

Development of an on-line preconcentration of copper(II) using the proposed microcolumn

The preliminary FIA system was then modified for the preconcentration and separation of trace copper(II) by using an on-line microcolumn packed with synthetic zeolite from natural perlite. An in-valve microcolumn was incorporated within the injection valve, by replacing the sample loop. While the valve was in "load" position, a sample solution passed through the column. When the injection valve was turned to the "inject" position, the eluent solution passed through the column to elute the sample into a stream of a mixture consisting of acetate buffer and nitroso-R solution. The absorbance of the complex was continuously monitored. The on-line system was optimized using the univariate method in order to determine the best chemical and flow conditions with good sensitivity. The recommended manifold and conditions are shown in Figure 2.2 and section 3.3.7 respectively. The calibration curve was linear over the range 0.02-0.16 mgCu(II)/l, which can be expressed by the regression equation $y = 245.3x + 0.0357$ (where x is the concentration of copper(II) in mg/l). The relative standard deviation is 0.98% (n=11) and recovery is 102% for determining 0.08 mgCu(II)/l. The detection limit was 0.007 mgCu(II)/l based on three times the standard deviation of replicate measurements. The proposed method was applied to the determination of copper(II) in drinking water and mining discharge water samples by comparing with standard addition method and ICP-OES respectively. The results obtained by the proposed method are not significantly different from those obtained by the reference method at confidence interval of 95% verified by student t-test.

The results obtained in this work shown that the proposed microcolumn packed with the synthetic zeolite from Lopburi natural perlite could be enhanced the detection limit of FIA spectrophotometric determination of copper(II) up to 100 times. It can be seen that the synthetic zeolite from natural perlite was a novel packing material for trace copper(II) determination. A further study will also aimed to investigate the analytical potentialities of the synthetic zeolite from natural perlite for on-line preconcentration of other trace heavy metals (e.g. Cd and Pb) in several environmental samples.