CHAPTER 4

CONCLUSIONS

In this research, three types of FI manifolds were designed and proposed for the preconcentration of trace chromium determination with different detectors including ICP-MS, FAAS and ETAAS. Firstly a procedure involving FI sorption and preconcentration for the off-line determination of some trace elements by ICP-MS has been described. Secondly, a flow injection on-line preconcentration system for determination and speciation of chromium in water samples with FAAS detection has been developed. Finally, a FI manifold with an WTAAS detection has been proposed for the on-line preconcentration, separation and determination of trace chromium in reference standard material samples. The separation and preconcentration procedure was focused on the molecular sorption principle. This approach based on the sorption of non-polar metal complexes onto the surface of the hydrophobic sorbent material. A sorbent made from PTFE material was mentioned. The sorbent also acted as a reactor which could be of different configurations, the serpentine and the knotted reactors were tested. The used of a PTFE beads packed column to replace the above reactors was also attempted.

4.1 A Comparison of Enrichment Factor of Knotted and Serpentine Reactors Using Flow Injection Sorption and Preconcentration for the Off-line Determination of some Trace Elements by ICP-MS

A knotted reactor (KR) made from PTFE tubing by tying interlaced knots is widely used as a sorbent unit for molecular sorption system. The mechanism of adsorption is assumed to be mainly the development of a sustained centrifugal force in the stream carrying the non-charged complexes, as a result of secondary flows created in the reactor. A serpentine reactor (SR) having a figure of 8 shape which can promote a secondary flow pattern as occurred in KR was interested to use as a new sorbent unit. The preconcentration efficiency of KR and SR was investigated for the FI molecular sorption preconcentration system. The preconcentration efficiency expressed as an enrichment factor (EF) was evaluated and compared. The FI system was tested for the determination of Cr(VI), Ni(II), Co(II), Cu(II), Zn(II), Mo(VI), Cd (II), W(VI) and Pb(II) with preconcentration as facilitated via formation and adsorption of the metal-pyrrolidine dithiocarbamate complexes (M-PDC) in acidic solution (0.001 M HNO_3) and sorbed onto the inner wall of the reactors. The adsorbed complexes were then eluated by 2%(v/v) HNO_3 and determined off-line by ICP-MS. Establishment of experimental parameters for optimization was initiated by finding the optimum length of the KR for preconcentration. The SR at the same optimum length of the KR was then prepared. The univariate method was used to find the optimum length of KR. The optimum length length which has sufficient capacity to accommodate all analyte complexes was found at 150 cm. Therefore, a 150 cm SR was then prepared. Under the same reactor length and optimum conditions for preconcentration, the EF gained in the KR was higher than that in the SR for all analytes under investigation. The EF of 4-36 and 3-12 were achieved using KR and SR, respectively. The results obtained indicate that the KR is preferable to use for the molecular sorption preconcentration system. It should be pointed out that the three dimensional configuration of KR created stronger secondary flow pattern than those in SR.

4.2 Flame Atomic Absorption Spectrometric Determination of Chromium(VI) and Total Chromium in Water Samples by FI On-line Preconcentration System Using Knotted Reactor

A KR was extended to incorporate into the FI on-line preconcentration system for determination of chromium(VI) and total chromium in water samples. Cr(VI) was separated and preconcentrated from Cr(III) by adsorption of Cr(VI) via complexation with APDC on the inner wall of the KR. The adsorbed complex was eluted by isobutyl methyl ketone (IBMK) and then analyzed by FAAS. The interfering ions were eliminated by adding 0.4% (w/v) EDTA into the sample solution. The total chromium was determined by FAAS after Cr(III) was converted to Cr(VI) by oxidation with potassium peroxydisulphate. Cr(III) can be calculated by difference. The complete oxidation of Cr(III) was performed with 0.001 M $K_2S_2O_8$ in 0.005 M H_2SO_4 for 30 minutes at 80 ^{0}C. The optimum condition for formation of Cr-PDC complex was studied by variable-size simplex method. The concentration of HCl and

APDC was found to be 0.15 M and 0.2% (w/v), respectively. The optimum PTFE KR length for sufficient adsorption efficiency was 125 cm.. With a preconcentration time of 180 s, the enrichment factor of 93.3 was gained. However, low retention efficiency of 11.9% was only obtained. The calibration curve was linear over the concentration range of 0.01-0.20 mg/l Cr(VI) with a detection limit (3 σ) of 0.004 mg/l Cr(VI). The sample throughput was 16 samples/h. The relative standard deviations were 3.13% and 2.14% for determining 0.025 mg/l and 0.10 mg/l Cr(VI) levels, respectively. The accuracy of the method was checked by analyzing total Cr in a SRM NIST-1640 and spiked water samples. The results obtained were agreed well with the certified values. The proposed method was further applied to the determination of Cr(VI) and total Cr in drinking water, mineral water and tap water samples. A reasonable recovery of the amounts added was found for all samples.

4.3 FI On-line Preconcentration of Low Levels of Cr(VI) with Detection by ETAAS. Comparison of Using an Open Tubular PTFE Knotted Reactor and a Column Reactor Packed with PTFE Beads

Although the KR has advantage of a low hydrodynamic impedance and allows high sample loading flow rates for obtaining high enrichment factor, the low retention efficiency on the inner wall of the KR restricts the significant improvement of its preconcentration capability. A column reactor packed with small PTFE beads was proposed for preconcentration of Cr(VI). The use of column reactor packed with PTFE beads was evaluated and compared to the performance of the open tubular

PTFE KR. It was tested for the determination of Cr(VI) with preconcentration as facilitated via formation and adsorption of the Cr(VI)-PDC complex, followed by elution of the complex by ethanol and ensuing detection the analyte by ETAAS. Establishment of experimental parameters for optimization was initiated by finding the optimum length of the KR. The PTFE beads packed column which offered a total surface area corresponding to the inner surface of KR at the optimum length was then prepared. The concentration of HCl and APDC for complex formation was optimized by variable-size simplex method. The optimum concentrations were found to be 0.015 M and 0.17% (w/v) for HCl and APDC, respectively. The optimum length of KR was 125 cm. A PTFE beads packed column of a length of 1.5 cm and loaded with 75 mg (100 μm) of PTFE beads was then made. This reactor had a total surface area corresponding to the inner surface area of the 125 cm long KR. The analytical performance of the KR and the packed column under the same optimum conditions were investigated. The proposed packed column offered a significantly sensitivity enhancement in term of limit of detection, enrichment factor and retention efficiency as compared with the conventional preconcentration procedure using a KR. Twice as high an enrichment factor (30.1) and retention efficiency (24.1%) were gained when using the column reactor. The limit of detection was also enhanced by a factor of 2, yielding a detection limit as low as 8.8 ng/l Cr(VI). In addition, the preconcentration method described has proven to be most reliable for determination of Cr(VI) in natural water and synthetic seawater samples. The results obtained indicate that the use of PTFE beads not only is a suitable packing material for the on-line sorption preconcentration system, but also is preferable to the use of KR

From the results obtained in this work, the use of column reactor packed with PTFE beads is expected to constitute an effective alternative for determination of various analyte in aqueous media via on-line sorption preconcentration procedures by intelligent chemistries involving different complexing and/or chelating agents-not the least because it offers significant potentials when employed in the recently described Lab-on-Valve format [127-129].