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FLOW INJECTION-FAAS DETERMINATION OF CHROMIUM, IRON, POTASSIUM AND SODIUM IN COMMERCIAL SWEETS WITH ON-LINE PRE-CONCENTRATION USING ION-EXCHANGE RESIN.

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Abstract: An on-line pre-concentration method based on flow injection ion-exchange analysis combined with flame atomic absorption spectrometry has been developed for the determination of chromium, iron, potassium and sodium in commercial sweets. Cation-exchange resin microcolumn has been used for pre-concentration of metals. Effect of flow rate on the binding and elution and pH for binding and molarities of eluting buffers for Cr, Fe, K and Na has been investigated.

Keywords: FIA ,FAAS, Pre-conentration, I0n-exchange resin, Metals, Sweets

INTRODUCTION

Pre-concentration of metal analytes in samples is required when concentration of metal ions is too low to be measured. Various workers[1-5] have pre-concentrated trace metals before determination. On-line pre-concentration of metals is an automatic method for enhancing the concentration. Materials such as charcoal[6-7], silica gels[8], ion-exchange resins[9-13] and solvent extraction[14] technique have been reported for pre-concentrating the metals. Motellier and Pitsch[15] have analysed some transition metals by ion-exchange chromatography using on-line pre-concentration technique.

In sweet samples, metals often occur at trace level. Their determination especially chromium is highly important because of health and safety reasons. Trace elements such as Sb, Pb and Tl are toxic and their determination have been carried out by various techniques[16-18]. In many cases enrichment step is necessary before instrumental determination of analytes in order to improve the sensitivity, precision and accuracy[19,20].

Ion chromatography is a common analytical tool for the determination of metals. However, it is not sensitive enough for determination of metals at trace levels in foods, sweets and biological fluids. Cation-exchange resins are highly sensitive towards transition metals and have been reported for trace analysis. In this work cation exchange resin packed microcolumn is used as an on-line pre-concentration for trace metals. In order to eliminate the interference of complex matrixes and to determine the metals automatically in sweet samples, a combination of flow injection analysis (FIA) set up coupled with flame atomic absorption spectrometer (FAAS) has been developed. The procedure requires injection of the sample on to the cation-exchange resin microcolumn (a component of FIA set up) followed by elution with 2M HCl and subsequent direct aspiration into the flame.

EXPERIMENTAL

Materials

All chemicals used were analytical grade. Cation-exchange resin was supplied by Rohm and Haas. Glassware used was from Pyrex. Deionized water used was supplied by Pak-Arab Fertilizer Ltd.,Multan, Pakistan.

Instrumentation

A flow sheet diagram of flow injection analysis set up connected to flame atomic absorption spectrophotometer (Hitachi Model A-1800) is shown in Fig.1. FIA manifold was comprised of connecting tubes, switching and injection valves (Rheodyne 5020, 125 μl volume) and a glass microcolumn (50 x 3 mm i.d., fitted with polyethylene end pieces with glass wool frits; Ominifit, UK.). It also contained a peristaltic pump (Cole-Parmer, Chicago). The pH

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measurements were made on Corning-125 pH-meter, calibrated with pH 4 and 9 buffers.

Sample Collection and Preparation

Different varieties of sweets were purchased from city market. Accurately weighed sweet samples (3 g) were treated by wet digestion method and then ashed completely in a muffle furnace (RJM 1.8 – 10, China) at 500°C for five hours. The ashed samples were dissolved in deionized water and filtered (Watman 42). Final volume was made up to 50 ml with 1% nitric acid.

Preparation of Solutions

1000-ppm stock solutions of chromium, iron, potassium and sodium were prepared from chromium (III) chloride hexahydrate, ferrous ammonium sulphate hyxahydrate, potassium chloride and sodium chloride. Salts were dissolved in 1% HNO_3 solution. The working standards were prepared from these stock solutions by appropriate dilution with 1% HNO_3. Matrix solution containing 200 ppm of calcium, 4 ppm of iron, 800 ppm of potassium and 300 ppm of sodium was also prepared[21]. However, the element under study was absent in respective matrix solution. One ml of matrix solution was added to 100 ml of each working standard solution.

Binding buffers of pHs 1.52, 3.37, 3.60, 8.89 and 10.51 were prepared from HCl (37%, sp.g. 1.19), 0.01 M CH_3COOH/0.01 M CH_3COONH_4 and 0.5 M NH_4OH/1 M NH_4Cl respectively. HCl was used as eluting buffer and molarities of 0.5, 1.5, 2.0, 2.5 and 3.00 were prepared.

Procedure

The binding and eluting buffer were alternatively pumped (9.92 ml/min) through the manifold (Fig. 1). Standard and sample solutions were injected through an injection valve into the carrier stream of binding buffer. The metal ions at a specific pH were exchanged by the ions on the resin while moving towards atomic absorption spectrometer and absorption intensity (peak height) was continuously recorded (Fig. 2). After elution of the bound peak, the carrier stream was switched back to the binding buffer.

RESULTS AND DISCUSSION

Effect of Flow Rate on Binding and Elution

To optimize the effect of flow rate on the binding peak and its subsequent elution by a buffer, flow rates of binding buffer were varied. Initially the flow rates of binding buffer (water) was kept constant and that of eluting buffer (2 M HCl) varied from 0.35 to 23.96 ml/min. It was observed that a slower flow rate of 0.35 ml/min gave maximum absorbance signals (Fig. 3). In order to improve the efficiency, i.e. no. of samples/min, without loosing much of the absorbance, a flow rate of 9.92 ml/min was opted. Further, keeping eluting flow rate constant, i.e. 9.92 ml/min, the flow rate of binding buffer was varied from 0.35 to 96 ml/min. Maximum absorbance signal was observed at a binding flow rate of 18.18 ml/min (Fig. 4). However, this flow rate was too fast to control because the joints in the FIA system became apart due to the backpressure developed within the system, and thus a compatible slower flow rate of 9.92 ml/min was chosen.

Effect of pH of Binding Buffer on Resin

In order to find the optimum pH for the binding buffer, molarity of eluting buffer, i.e. 2M HCl, was kept constant and the binding pH for Cr, Fe, K and Na on to resin was varied from 1.52 to 10.51. Fig. 5 shows the optimum pH for chromium, 3.6; iron, 6.72; potassium, 3.7; and sodium 3.60 and 7.46. The working pH for sodium was selected 7.46 instead of 3.60 without loosing much of the absorbance intensity because water was plentiful and cheaply available.

Effect of Molarities of Eluting Buffer on Resin

Keeping pH of binding buffer constant, i.e. 3.60 for Cr, 6.72 for Fe, 3.70 for K and 7.46 for Na, molarity of eluting buffer, i.e. HCl, was varied from 0.5 to 3.0 M in order to elute the binding peaks for Cr, Fe, K and Na. The effect of molarities of eluting buffers on the elution of binding peaks is shown in fig. 6. The optimum molarity of eluting buffer, i.e. HCl, was two molar for chromium, potassium and sodium and three molars for iron.

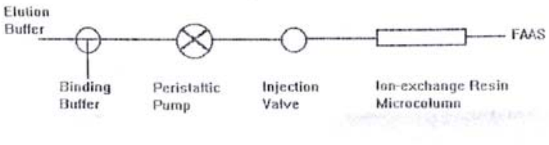

Fig.1 Flow Injection Manifold

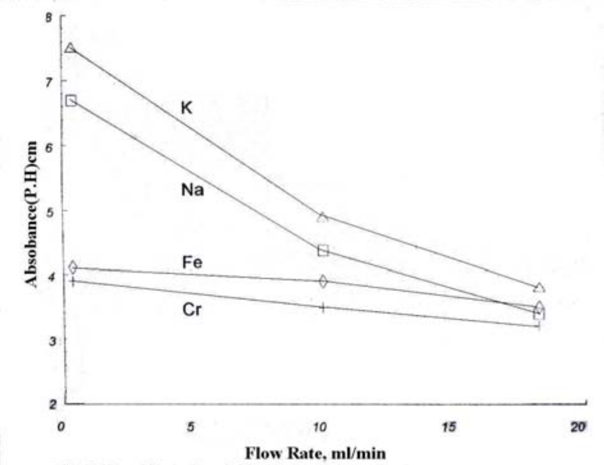

Fig.3 The effect of variable elution at constant binding flow rate for Cr,Fe,K and Na

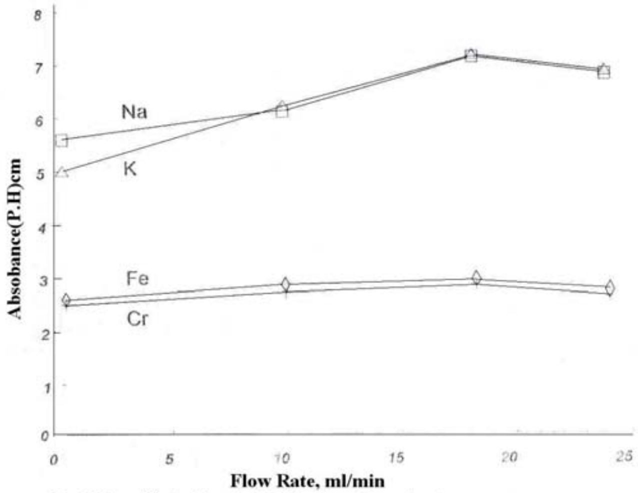

Fig.4 The effect of variable binding at constant elution flow rate of Cr, Fe, K and Na

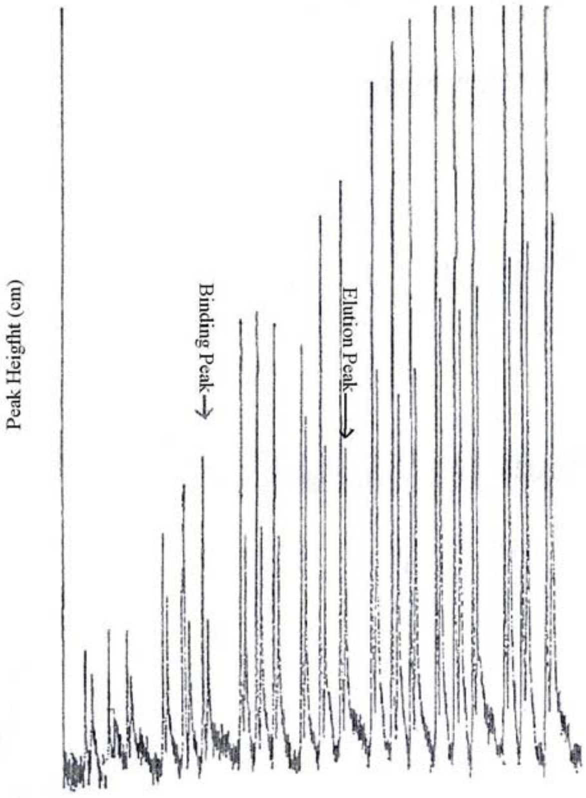

Fig.2 Absorbance print out obtained by injecting Ferrous Ammonium Sulphate solution in the concentration range 5 to 35 ppm.

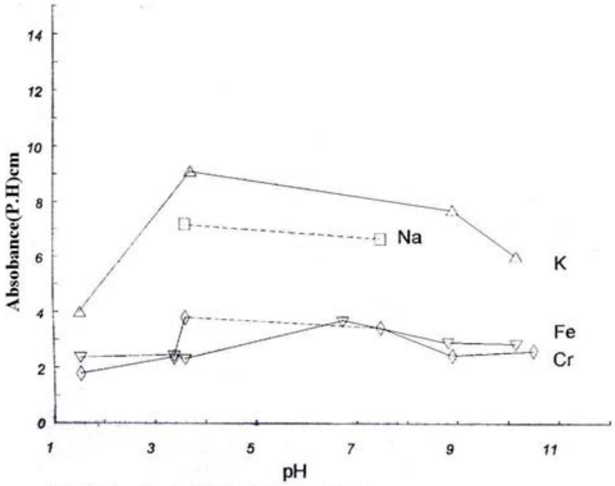

Fig.5 The effect of pH of binding buffer on the elution of Cr, Fe, K, Na

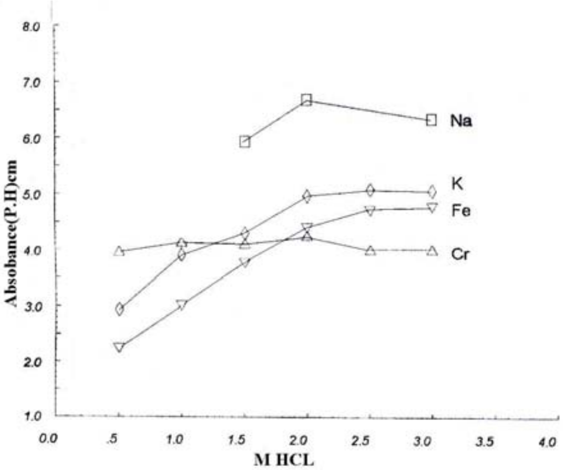

Fig.6 The effect of elution buffer on the binding peak height of Cr, Fe, K and Na

Application to Analysis of Sweet Samples

Different varieties of commercial sweets were collected from city market. They were grouped as candies and toffees. These samples were subjected to sample preparation treatment as described in experimental and analysed for Cr, Fe, K and Na by FIA-FAAS detector. The calibration curve for each metal was linear and relevant analytical parameters are listed in Tables 1 & 2. The analytical data for metals found in sweet samples is given in Table 3. The K and Na being higher in quantity are reported as mg/g and that of Cr and Fe being very low as μg/g.

Table 1 Instrumental Parameters Used for the Determination of Cr, Fe, K and Na by FAAS

Element	Cr	Fe	K	Na
Wavelength (nm)	357.9	248.3	766.5	589
Slit Width (nm)	1.3	0.2	2.6	0.4
Lamp Current (mA)	7.5	10	10	10
D2 Background	Off	Off	Off	Off
Air Flow Rate (1/min)	9.5	9.5	9.5	9.5
Acetylene Flow Rate (1/min)	2.6	2.3	2.3	2.2
Burner Height (mm)	7.5	7.5	7.5	7.5

Table 2 Parameters of Calibration Curve

Name of Element	Slope	Correlation Coefficient	Intercept	Standard Error
Chromium	0.4000	0.9996	0.7516	0.1117
Iron	0.2886	0.9958	0.9512	0.3462
Potassium	0.1762	0.9981	1.5190	6.9×10^{-2}
Sodium	0.1718	0.9725	2.2696	0.2580

Table 3 Concentration of Cr, Fe, K and Na in Commercial Sweets

Sample	Cr (μg/g)	Fe (μg/g)	K (mg/g)	Na (mg/g)
Candies Rus Candy	72.082	76.793	0.22	0.452
Crunchi Bar	43.332	57.739	5.540	4.074
Mentholated Havet	35.832	42.149	1.986	5.494
Kino	37.499	45.036	0.262	1.572
Butter	41.666	47.920	0.217	0.553
Milk	30.416	50.811	2.143	3.536
Toffees Chocolate	36.66	51.965	0.422	1.901
Creamline	40.832	48.154	0.375	3.638
Milk	38.749	49.078	3.073	2.3
Milk	40.000	53.697	2.805	2.765

The analytical data of sweet samples suggests that potassium varies from 0.217 to 3.013 mg/g and sodium from 0.452 to 5.494 mg/g. However, the observed quantity of chromium and iron in different sweet samples is 30.416 to 72.082 μg/g and 42.149 to 76.793 μg/g respectively.

CONCLUSION

Sweet samples were analysed for metal ion concentration by FIA technique using a cation-exchange resin microcolumn for pre-concentration coupled with FAAS detector. Factors such as effect of flow rate of binding/elution buffers, pH of binding buffer and molarities of eluting buffer that affect peak height (cm) of binding metal ions on to the resin have been studied. Standard and sample solutions were injected on to the microcolumn of the FIA system and absorbance intensity in peak height of binding metal ions were recorded. Using standard calibration curves, concentrations of Cr, Fe, K and Na have been determined in sweet samples as given in the Table 3.

The concentration of K and Na is comparatively high while that of iron and chromium is low except in one sample, i.e. rus candy where chromium is 72.082 µg/g. The usual, adult, daily intake of chromium, iron, potassium and sodium in the USA is 5 - 150µg, 10 – 30 mg, equivalent to 10 g of NaCl and 3.7 – 7.5 g of KCl respectively[22].

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