DETERMINATION OF CYANIDE AND THIOCYANATE ANIONS BY FLAME ATOMIC ABSORPTION SPECTROMETRY IN A FLOW SYSTEM USING AN ON-LINE PRECONCENTRATION TECHNIQUE

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Abstract

A flow injection atomic absorption spectrophotometric (FI-AAS) method is described for determination of cyanide and thiocyanate. The method involves first the precipitation of the analyte with silver nitrate in a Tygon tube, containing small glass beads, connected to the atomic absorption spectrophotometer and then passing a suitable dissolving agent which dissolves the precipitate and carries it with its cation content to the nebulizer of the AAS to be detected. Various parameters such as concentration of chemical reagents, flow rate of solutions and other AAS variables were optimized. Detection limits were 3×10^{-6} and 1×10^{-6}M for CN$^-$ and SCN$^-$, respectively when $S_2O_3^=$ and CN$^-$ solutions are the respective dissolving agents with a sample throughput of about 18/hr and 16/hr for CN$^-$ and SCN$^-$, respectively.

The development of rapid methods with low detection limits for determination of some anions is important especially in industrial processes and biological fluids. Cyanide is a toxic material and there should be an accurate and rapid method for its detection and therefore a lot of reports

appeared recently concerning its determination. Thiocynate is also present in wastewater and biological fluids as a major metabolite of cyanide and therefore its determination is necessary for monitoring its level.

Several methods have been reported for thiocynate determination but very few of them can be used for detection of trace amounts. The most widely used methods are those based on spectrophotometry[1-6], which include either the formation of a red complex with iron (III) ions or the Konig synthesis of pyridine dyes. Flow injection analysis (FIA) technique based on spectrophotometric methods of detection have been developed for thiocynate determination[7-9]. Other methods, as ion chromatography[10,11] cathodic stripping voltammetry[11] and linear sweep polarography[13] have been used for thiocynate determination.

Cyanide determination has been achieved by several methods. The most important are those based on spectrophotometry[13-15]and potentiometry[16,17]. Indirect methods of analysis using AAS technique have been recently developed for cyanide determination[18-20]. The methods involve the conversion of cyanide to a species that can be detected by AAS.

FI-AAS technique has a widespread use nowadays due to its simplicity, high frequency in measurement, minimum reagent consumption and the possibility of automating sample preparation and analysis. Analysis of some cations[21] and anions[22,23] has been achieved by FI-AAS technique using an on-line preconcentration unit. The cation and the anion are allowed to precipitate for a period of time and then the precipitate is dissolved by a certain dissolving agent which carries it to the AAS to be detected. In this work the analyte is precipitated by silver nitrate and allowed to preconcentrate for

two minutes before a dissolving agent is allowed to pass which dissolves the precipitate and carries it with its cation content to the AAS to be detected. From the absorbance of the silver, which is proportional to the anion concentration, the analyte concentration can be calculated.

Experimental

Apparatus:

A Perkin-Elmer 372 atomic absorption spectrophotometer with a silver hollow-cathode lamp (4mA) and strip chart recorder with a 20mV output were used for the FIA measurements. The wavelength was 328.1 nm, acetylene and air flow rates were 1 and 8 L.min^{-1}, respectively and the slit width was 2 nm. Teflon tubing of 1 mm i.d. from Beckman Altex was used in the flow system. Two Rheodyne loop injection valves were used to introduce either the washing or the dissolving solution to the precipitating loop. The length of the mixing coil was 5 cm with 1 mm i.d. The precipitating loop was a Tygon tube (7 cm long and 2.8 mm i.d.) filled with small size pyrex glass beads (1.9 mm in diameter from Thomas Scientific) which is connected vertically to the injection valve and connected to the nebulizer of the atomic absorption spectrophotometer via a Teflon tube (Figure 1). The void volume of the precipitating loop was found to be 85 µl. A peristaltic four channel pump is used to draw the cation and anion solutions into the precipitating loop and then to the waste and the negative pressure from the nebulizer was used to draw the washing and dissolving agents through the precipitatingt loop to the nebulizer of AAS. The dissolvant flow rate was coarsely controlled by adjusting the nebulizer of the AAS.

Reagents:

All reagents were of analytical reagent grade. Solutions were prepared in distilled, deionized water. All standard solutions of silver (AgNO$_3$) were prepared by appropriate dilution of 1000 ppm stock standards. Cyanide and thiocyanate standard solutions were prepared by dissolving KCN and KSCN (Merck), respectively, in deionized water to produce 1g/ℓ solutions. Working solutions were prepared by appropriate dilution with deionized water. Sodium thiosulfate was of analytical grade from BDH Chemicals Ltd and ammonia solution 30% in water was from Fluka-AG-Chem Fabrik.

Procedure:

Standard solution of the analyte (CN$^-$ or SCN$^-$) and silver nitrate solution were passed through the flow system as shown in the manifold in Figure 1. The two solutions mix in the mixing coil and then are pumped to the precipitating loop. The precipitation was allowed to occur for 2 minutes and the excess amount is pumped to the waste. The selecting valve (injector II) allows first a stream of the washing solution (deionized water) to pass to the precipitating loop and after that the dissolving agent is allowed to pass, which dissolves the precipitate and carries it, with its cation content, to the nebulizer. The produced FI-AAS signal, which is proportional to the cation concentration and in turn proportional to the anion concentration, is recorded. The concentration of silver ion used is 750 and 600 ppm for the cyanide and thiocyanate determination, respectively. The dissolving agent concentration was varied until the optimum concentration of it needed for complete dissolution was determined (0.10 M NH$_3$, 0.05 M S$_2$O$_3^=$ and 0.04 M CN$^-$
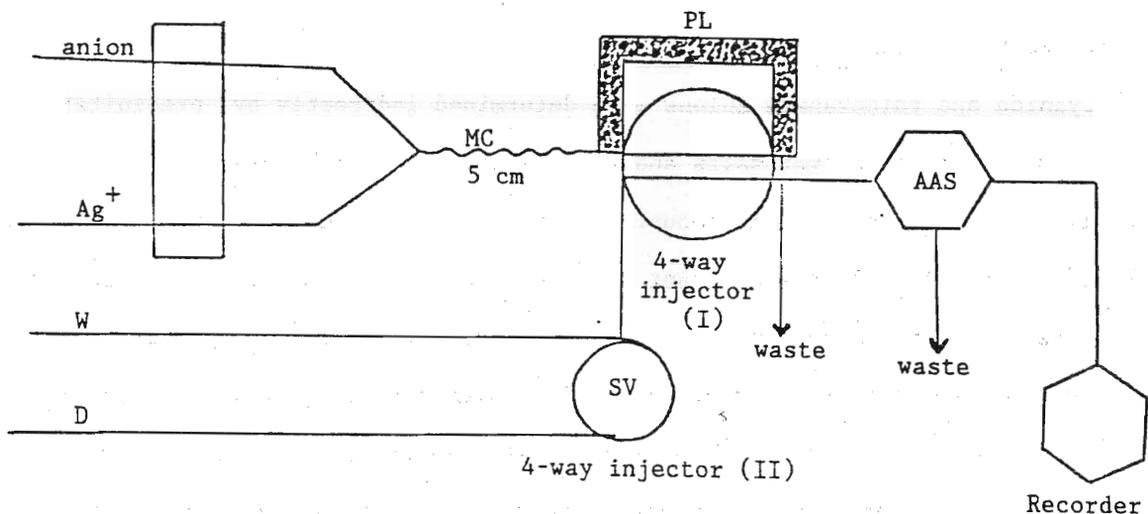
Figure 1: Schematic diagram of the flow-injection system for the determination
of cyanide and thiocyanate: MC, mixing coil; PL, precipitating loop;
W, washing stream; D, dissolving solution and SV, selecting valve.
Flow rates of the anion and cation are 1.5 and 1.0 ml.min^{-1} in case
of cyanide determination and 1.2 and 1.0 ml.min^{-1} in case of
thiocyanate determination. Dissolving agent and washing solution
flow rates are 2.1 and 2.3 in case of cyanide determination and 1.8
and 1.4 ml.min^{-1} in case of thiocyanate determination.

in case of SCN^- determination and 0.4 M NH_3 and 0.025 M $S_2O_3^=$ in case of CN^-

determination) and was adopted through this work. The preconcentration was

allowed to occur for a period of time (1-30 minutes) to enhance preconcentra-

tion. The time for washing silver cyanide and silver thiocyanate is 30 and 50

S, respectively. Dissolution of silver cyanide requires 35 and 32 S when NH_3

and $S_2O_3^=$ were the respective dissolving agents for 1.3×10^{-4} M of CN^- solu-

tion. Silver thiocyanate dissolution time was 48, 45 and 37 S when $S_2O_3^=$, NH_3

and CN^- were the dissolving agents, respectively, at 1.1×10^{-4} M SCN^-.

Result and Discussion:

Cyanide and thiocyanate anions were determined indirectly by precipitating them as their silver salts and then dissolution of the precipitate by a certain dissolving agent. The amount of precipitate formed in a constant time period is proportional to the amount of anion under the experimental conditions used. Precipitation was allowed to occur for a period of time (1-30 minutes) to enhance preconcentration and it is found that up to 18 minutes in case of CN^- and 21 minutes in case of SCN^- determination, there is an increase in signal with increase in preconcentration time which then levels off. This is believed to be due to the dissolving agent saturation. To remove the excess of silver ions, the precipitate was washed by passing deionized water through the precipitate until nil signal for silver was obtained. The effect of silver ion concentration on the signal is studied. For a 5×10^{-5}M cyanide solution it is found that a 750 ppm silver gives the maximum response, whereas for 7×10^{-5}M thiocyanate solution, 800 ppm silver solution is required for maximum response. The dissolving agent concentration was also varied until the concentration required for complete dissolution was found. For dissolution of AgCN precipitate, 0.4 M NH_3 and 0.025 M thiosulfate were used, whereas for AgSCN dissolution 0.01, 0.05 and 0.04 M of NH_3, $S_2O_3^=$ and CN^-, respectively, were required.

The effect of flow rate of chemical reagents on the silver response was studied. Changing the flow rate of silver ion and analyte solution in the range 0.90 - 5.5 ml/min causes the signal to increase linearly with increase in flow rate. Figure 2 shows calibration curves for SCN^- determination using different flow rates and using CN^- as dissolving agent. It is observed that
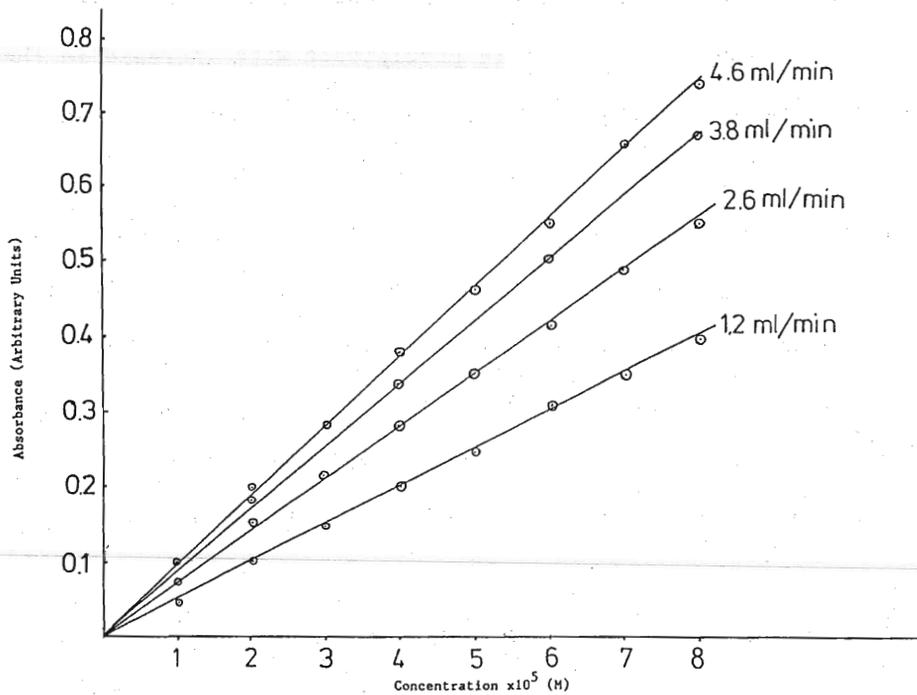
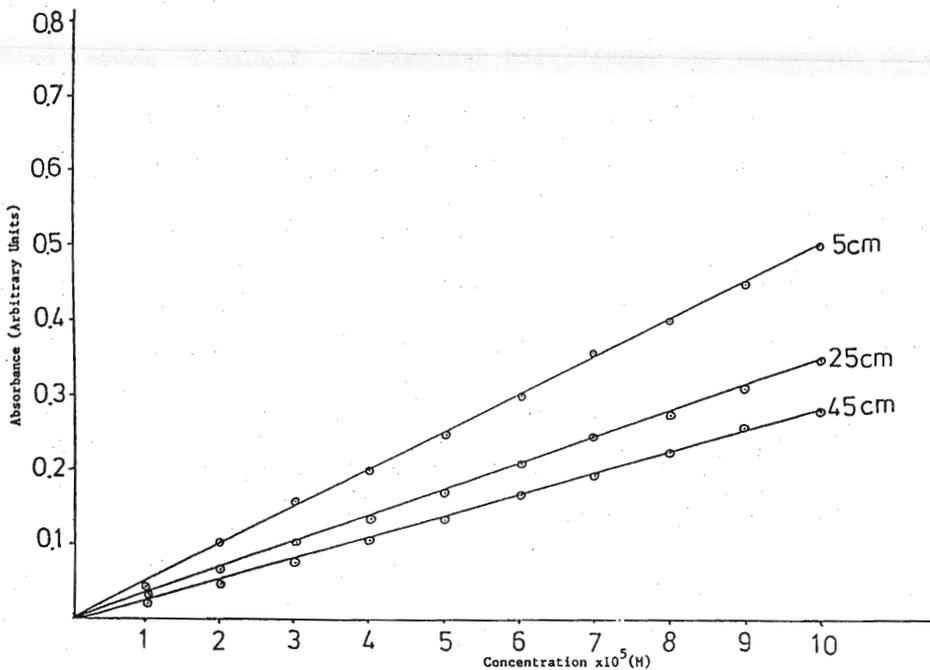Figure 2: Calibration curves for SCN⁻ determination at different flow rates.

Figure 3: Calibration curves for SCN⁻ determination using mixing coils of different lengths.

with increase in flow rate the response increases, since more silver ions mix with more analyte ions to form more precipitate with increase in the flow rate. The same behaviour was observed in case of CN^- determination. Flow rates of 1.0 for Ag^+, 1.2 for SCN^- and 1.5 ml/min for CN^- are chosen in this work which give sufficient sensitivity and reasonable reagent consumption. If more sensitivity is required, the flow rate can be increased. The dissolving agent flow rate was also optimized in order to get sufficient sensitivity and good reproducibility. It is found that the signal increases exponentially with increase in flow rate of the dissolving agent and therefore 2.1 and 1.8 ml/min were chosen in this work in case of CN^- and SCN^- determinations, respectively.

The effect of the length of the mixing coil on the signal was studied. It is found that in both determinations (CN^- and SCN^-), the signal decreases with increase in coil length which indicates that with increase in coil length dispersion increases and sensitivity decreases. Figure 3 shows calibration curves for SCN^- determination using different coils of different lengths. The same behaviour was observed in case of CN^- determination.

The effect of changing the dimensions of the precipitating loop on the signal was studied. Precipitating loops of different lengths (5, 7, 10, 15, 20 cm) were tried and it is found that those longer than 7 cm cause broadening of the signal whereas those shorter than 7 cm is difficult to fit through the injection valve. Precipitating loops of larger diameter than 2.8 mm (3 and 3.5 mm i.d.) have no effect on the signal but cause some loss in

reproducibility and require more time for dissolution and washing, therefore 7 cm length and 2.8 mm in diameter were the dimensions of the precipitating loop which was used in this work.

Figures 4 and 5 show calibration curves for SCN^- and CN^- determination, respectively, at the optimum conditions. The linear upper limit at 1.4×10^{-4}M SCN^- and 1.7×10^{-4}M CN^- are believed to be due to loop saturation. Cyanide as dissolving agent causes the highest sensitivity in case of SCN^- determination and in case of CN^- determination, $S_2O_3^{2-}$ gives the highest sensitivity. Different enhancements in sensitivity according to the type of dissolving agent was observed previously in silver determination[20] where $S_2O_3^=$ as dissolving agent caused higher sensitivity than CN^- or NH_3. The different sensitivities obtained by different dissolving agents is probably due to difference in rate of dissolution in addition to different abilities of complex formation. In case of CN^- determination, $S_2O_3^=$ dissolves the precipitate in 32S compared to 35S when it is dissolved by NH_3. In addition to that, $S_2O_3^=$ is a stronger complexing agent toward silver than NH_3. In case of SCN^- determination, 37S are required for dissolution when CN^- is the dissolving agent, whereas 45 and 48S are required when NH_3 and $S_2O_3^{2-}$ are the respective dissolving agents.

The detection limit and precision of the method at the optimum conditions are listed in Table I. It is clear that using this method sufficient sensitivity and lower detection limits than previously reported procedures, can be achieved.
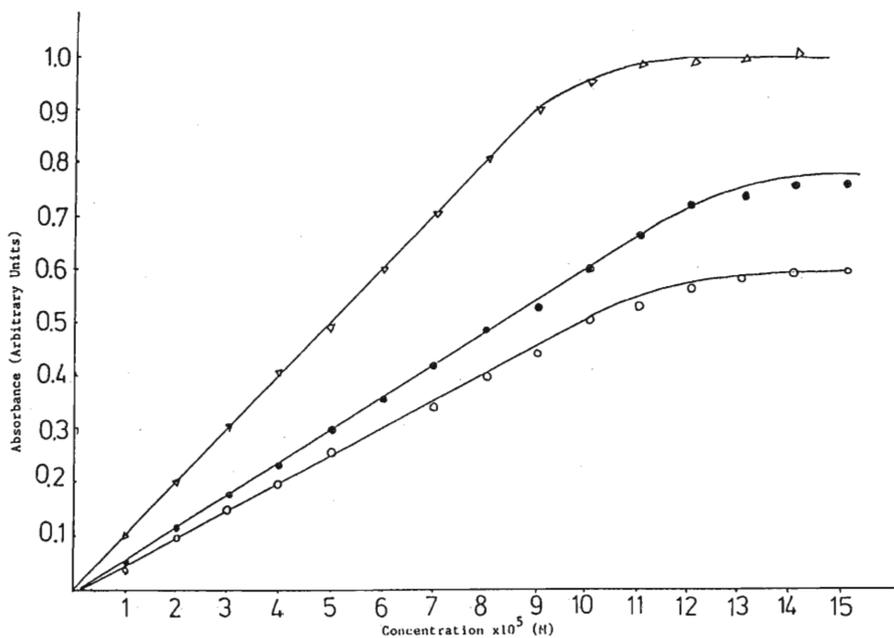
Figure 4: Calibration graphs for SCN⁻ determination at the optimum conditions using NH_3 (o), $S_2O_3^=$ (•) and CN⁻ (△) as dissolving agents.
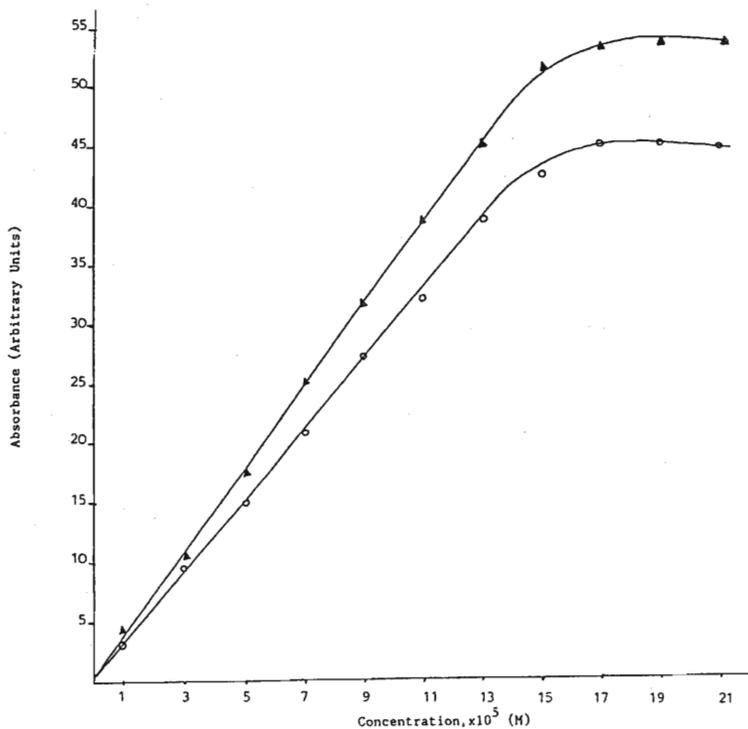
Figure 5: Calibration curves for CN⁻ determination at the optimum conditions using NH_3 (o) and $S_2O_3^=$ (▲) as dissolving agents.

Table I: Analytical Performance of the FIA-AAS Technique for Determination of Cyanide and Thiocyanate.

Analyte	Dissolving Agent	Detection[a] Limit (M)	RSD(%)[b]
CN^-	$S_2O_3^=$	3×10^{-6}	1.4
	NH_3	5×10^{-6}	1.7
SCN^-	CN^-	1×10^{-6}	1.5
	NH_3	6×10^{-6}	1.2
	$S_2O_3^=$	1×10^{-5}	1.0

a: Detection limit, calculated as the concentration corresponding to three times the base line noise.

b: Relative standard deviation at 6×10^{-5}M SCN^- and 7×10^{-5}M CN^- standards for ten replicate measurements.

Figures 6 and 7 show the signals obtained for CN^- and SCN^- standards at the optimum conditions. Considering the preconcentration, the washing and dissolution time, the method results in a sampling frequency of about 18 and 16/hr in case of CN^- and SCN^- determinations, respectively.
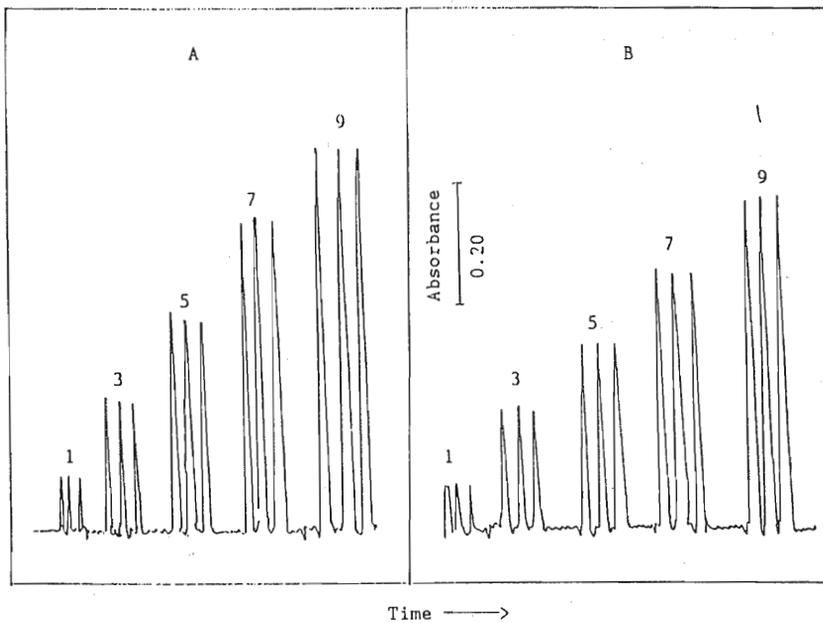
Figure 6: Calibration runs for determination of CN^- using (A) NH_3 and (B) $S_2O_3^=$ as dissolving agents (Concentration in M x10^5).
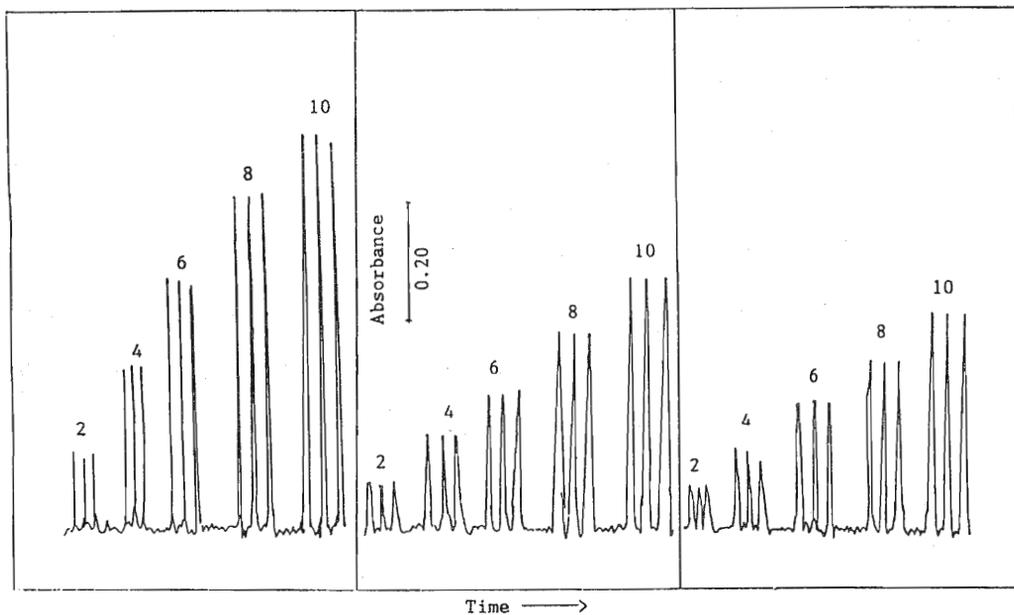

Figure 7: Calibration runs for determination of SCN^- using (A) NH_3, (B) $S_2O_3^=$ and (C) CN^- as dissolving agents (Concentration in M x10^5).

Table II. Effect of Foreign Anions on the Determination of Cyanide
$(5 \times 10^{-5} M)$ and Thiocyanate $(2 \times 10^{-5} M)$. Foreign Anions Were
Added in 20-fold Amount.

Ions Added	Added as	Relative error(%)	
		CN^-	SCN^-
acetate	CH_3COONH_4	0.5	0
formate	HCOONa	1	1.5
iodate	$NaIO_3$	2	1.7
flouride	NaF	3	2.9
sulfite	Na_2SO_3	2.8	1.4
sulfate	Na_2SO_4	1.5	0.2
citrate	sodium citrate	4	2
oxalate	$(NH_4)_2C_2O_4$	12	13
carbonate	Na_2CO_3	0.9	1.2
phosphate	Na_3PO_4	15	10
chromate	K_2CrO_4	29	32

Interferences

The effect of some foreign anions were investigated and it is shown in
Table II. The absorbances of a $5 \times 10^{-5} M$ solution of cyanide or thiocyanate was
compared with that produced by a similar solution containing in addition $1 \times 10^{-3} M$
(20-fold) of foreign anion. The presence of anions such as fluoride,

iodate, formate, bromate, nitrite, nitrate and acetate cause less than 3% error in absorbance, whereas anions that can form insoluble precipitates with silver as Cl^-, Br^-I^-, $CrO_4^=$ and $CO_3^=$ interfere seriously if present.

Conclusion:

Cyanide and thiocyanate anions can be determined indirectly using the FI-AAS technique. The method is simple, precise and rapid. Due to an increase in pollution problems, this method has a potential practical application for controlling pollutants in wastewater. Compared with other methods, this method is more sensitive, easier and there is no need for changing the precipitating loop since it is cleaned by passing the dissolving agent for a short period of time. The sensitivity can be increased, if more preconcentration time and higher flow rates are used.

Acknowledgements:

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