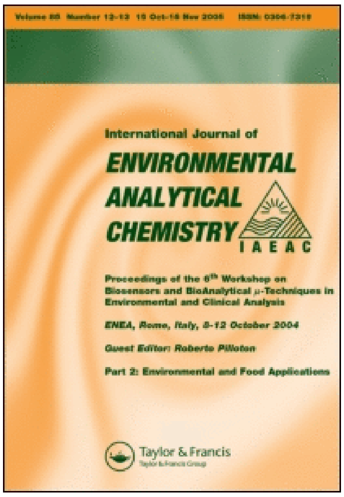

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Assessment of Infrared Spectroscopy for Detecting Cyanide Species in Aqueous Solutions

A. D. Stuart[a]; R. Van Den Heuvel[a]
[a] BHP Research - Newcastle Laboratories, Wallsend, NSW, Australia

To cite this Article Stuart, A. D. and Heuvel, R. Van Den(1992) 'Assessment of Infrared Spectroscopy for Detecting Cyanide Species in Aqueous Solutions', International Journal of Environmental Analytical Chemistry, 49: 3, 171 — 181
To link to this Article: DOI: 10.1080/03067319208027568
URL: http://dx.doi.org/10.1080/03067319208027568

Intern. J. Environ. Anal. Chem., Vol 49, pp. 171-181
Reprints available directly from the publisher
Photocopying permitted by license only

ASSESSMENT OF INFRARED SPECTROSCOPY FOR DETECTING CYANIDE SPECIES IN AQUEOUS SOLUTIONS

A. D. STUART and R. VAN DEN HEUVEL

BHP Research - Newcastle Laboratories, P.O. Box 188, Wallsend NSW 2287, Australia

(Received, 19 September 1991; in final form, 20 February 1992)

The potential of infrared spectroscopy for detection and speciation of cyanides in aqueous solution has been assessed. The non-invasive technique has good prospects for speciation of many metal cyanides and other cyaniferous ions, and sensitivities of 10-100 mg l^{-1} can be achieved readily. An additional species, thought to be an aquo- or hydroxo-cyano complex, was observed to be present in association with ferricyanide ion in strongly alkaline solutions.

KEY WORDS : Cyanide complexes, cyanate, thiocyanate, wastewater, infrared spectroscopy.

INTRODUCTION

Cyanide is an environmentally important species, due to its toxicity, and it is a legal requirement that cyaniferous effluents be monitored on a regular basis. The levels of both free and total cyanide are significant.

Because of its complicated chemistry, measuring cyanide is not trivial[1]. Conversions to cyanate (OCN^-) and thiocyanate (SCN^-) readily occur through reaction with oxygen and sulfides, respectively. In addition, cyanide in aqueous solution readily combines with many metal ions to form metal-cyanide complexes. These range greatly in their stability; some complexes can be isolated as stable salts, others exist only in solution under certain conditions (of pH, etc).

The effective management of cyanide solutions, either in process streams or in waste streams, depends upon knowledge of the metal-cyanide complexes that are present. For example, waste streams containing stable complexes may require more intensive treatment to ensure destruction of all the cyanide present.

Although techniques such as polarography can be used for rapid determination of free cyanide in solutions[2], the analysis for total cyanide is time-consuming, requiring the prior destruction of all forms of complexed cyanide that may be present. The speciation of the various metal-cyanide complexes in a sample is even more difficult and laborious. Stable

Table 1 Peak Positions for Selected Metal Cyanide Species[7]

Compound	*Peak Position (cm^{-1})*	*Compound*	*Peak Position (cm^{-1})*
$[Fe(CN)_6]^{4-}$	2033	$[Co(CN)_6]^{3-}$	2129
$[Cu(CN)_4]^{3-}$	2094	$[Pt(CN)_4]^{2-}$	2133
$[Fe(CN)_6]^{3-}$	2118	$[Ag(CN)_2]^{-}$	2135
$[Ni(CN)_4]^{2-}$	2123	$[Pd(CN)_4]^{2-}$	2136
$[Cr(CN)_6]^{3-}$	2128	$[Au(CN)_2]^{-}$	2145

species such as iron, gold and cobalt cyanides can be measured by laboratory-based chromatographic techniques such as high performance liquid chromatography (paired ion chromatography)[3,4]. Although similar approaches have been pursued for the less stable species[3,4], in fact the measurements disturb the equilibria of the overall system and what is measured is not necessarily the true situation.

Rapid, non-invasive techniques would be preferred for the characterisation of cyaniferous solutions. A possible approach is to use infrared spectroscopy; only optical access to a sample is needed. It is known that inorganic cyanide complexes have characteristic infrared (IR) spectra in both the solid form[5-7] and in aqueous solution[7]. Included among the absorption bands in the IR spectra of the complexes are strong bands around 2000-2200 cm^{-1} and weaker bands in the 200-500 cm^{-1} region, assigned to CN vibrations[6,7].

Prior work on IR measurements of CN complexes in aqueous solution has been mainly concerned with the derivation of structural information about the complexes[7] (e.g. tetrahedral, square planar or octahedral coordination of CN ligands around the metal). This information can be obtained from consideration together of the IR and Raman spectra of the complexes.

Most of the transition metal complexes have been studied by IR; Table 1 (extracted from reference 7) details the measured position of the main CN stretching vibration for some of the more important metals.

Relatively concentrated solutions have been used in the IR studies, since the aim was to obtain detailed spectral information. However, the CN absorption is a strong one, so the IR method was potentially of reasonable sensitivity. Given the potential for speciation, it was therefore of considerable interest to examine the detection sensitivities for metal cyanide complexes and for other cyanide species (CN, SCN, OCN) that could be obtained within practical limits. This report describes the investigation of the potential of IR as a non-invasive sensor for cyanide species.

EXPERIMENTAL

Infrared spectra were recorded using a Nicolet 60SX FT-IR spectrometer operating with mid-IR optics. Successive scans were co-added until the required signal-to-noise levels were achieved; typical acquisition times were around 10 minutes (2500 scans). Spectra were recorded with 8 cm^{-1} resolution.

Some preliminary work was carried out using a Barnes ZnSe ATR (attenuated total reflectance) cell as it was thought that the strong water bands present in the spectra would prevent the use of conventional IR cells. Measurements were made using a solution of Na_2CO_3 (selected because of its better stability and hence easier handling). A strong peak at 1260 cm^{-1} was readily evident; the limit of detection was around 120 mg l^{-1} (as CO_3^{2-}).

Transmission levels through the ATR cell at water absorption bands around 2000 cm^{-1} were quite high, suggesting that much greater pathlengths could be used. Accordingly, further work in the study was carried out using conventional IR cells.

Cell pathlengths of 0.1, 0.25, 0.5 and 1.0 mm were investigated; only the 0.1 mm pathlength was suitable as insufficient signal was present at the detector with larger pathlengths. Initially, difficulties were encountered in using this cell due to the presence of strong interference fringes. The source of these was attributed in part to difficulties in completely removing small bubbles within the cell. A flow-through arrangement was subsequently used; this was convenient for general operations and also provided an efficient flushing system.

Compositions of "unknown" sample mixtures were derived by using the spectra of samples of known concentration as reference. Partial least squares (PLS) software (version Nicolet PLS Quant) was used to derive appropriate regressions for the suite of reference samples, and the results applied to the "unknowns". Detection limits were estimated from assessment of the precision obtained by this process. PLS is a full spectrum quantitative analysis technique which involves iteratively estimating a linear combination of spectral features in the reference set such that concentrations are optimally predicted.

Solution Matrix

Preliminary screening of some CN solutions confirmed the studies in the solid state[5] that the peaks of principal interest occur around 2100 cm^{-1}. Unfortunately, this region coincides with a strong water absorption (OH stretching vibration); this is an intrinsic limitation to the sensitivity of the measurement because:

—The strong water absorption band limits the optical pathlengths that can be used in the cell, and

—Slight variations in band intensity (e.g. due to changes in density, temperature, pH, etc) compared with the spectrum of the reference solution will not ratio out and hence will have an effect on the measurement.

In order to simplify the study, matrix effects were minimised by using only a stock solution of KOH (1.0 g l^{-1}, pH 12.3) for preparation of samples and for the reference solution.

Table 2 IR Absorption Bands for Selected Cyanide Species

Compound	*Reported Peak* (cm^{-1})	*Measured Peak (cm-1)*	*Comments*
$[Fe(CN)_6]^{2-}$	2033	2036	
$[SCN]^-$		2064	
$[CN]^-$		2078	
$[Cu(CN)_4]^{3-}$	2094	2092	Additional peak at 2168 cm^{-1}
$[Fe(CN)_6]^{3-}$	2118	2115	Additional peak at 2036 cm^{-1}
$[Au(CN)_2]^-$	2145	2146	
$[OCN]^-$		2168	

RESULTS

Studies of Cyanide Species Detection

The measured infrared band positions for a number of species in solution are reported in Table 2. Good agreement was found with literature reported positions[7]. The IR spectra of the copper cyanide and ferricyanide solutions each contained an additional absorption band. The band at 2168 cm^{-1} in the copper cyanide solution corresponded in position with cyanate ion, and it was assumed that some oxidation had taken place during preparation of the solution. The band at 2036 cm^{-1} in the ferricyanide solution corresponded in position with the band for ferrocyanide ion; however, subsequent investigations suggested that this was not the explanation for the additional band. This is discussed further below.

Subsequent analyses of spectra were carried out using PLS software. For each species, a range of concentrations in solution were prepared and the spectra recorded. The PLS software was then used to calculate the best fit of spectra with concentrations. As shown in Table 3, excellent correlations were observed in all cases.

The predictive capabilities were also examined for some species (see Table 3); once again, very good correlations were observed. Verification studies were only carried out for some species; the results are considered to be indicative for predictions generally.

Mixtures of cyanide and thiocyanate were next examined, as an indication of the performance of the partial least squares IR method in dealing with speciation within mixtures. This pair was selected because, of those species used in the study, it appeared the most difficult to handle:

—the SCN and CN absorption bands were very close together (2064 and 2078 cm^{-1}, respectively), and

—the relative absorptivity for the SCN band was around four times that for the OCN band.

The performance of the PLS infrared method on the mixture was also very encouraging; results are shown in Table 4. As can be seen, the PLS software allowed concentrations in the range 0-100 mg l^{-1} for SCN and 0-1000 mg l^{-1} for CN to be derived to within 5 mg l^{-1} for SCN and 40 mg l^{-1} for CN.

Table 3 Partial Least Squares Analysis of Spectra

Species	*Comments*	*Actual Concn(mg l^{-1})*	*Concn From Calibn Fit*	*Predicted Concn*	*Correlation Coefficient (R^2)*
#$[Fe(CN)_6]^{4-}$	Calibration Set	4	4		R^2=0.999
		13	13		
		50	50		
		51	50		
		53	53		
		86	88		
		409	409		
	Verification Set	6		6	R^2=0.983
		17		17	
		22		22	
		23		20	
		16	13		
#$[Au(CN)_2]^-$	Calibration Set	21	21		R^2=0.999
		33	35		
		67	69		
		98	98		
		129	128		
	Verification Set	28		32	R^2=0.999
		50		50	
		91		82	
$[OCN]^-$	Calibration Set	5	5		R^2=0.999
		23	25		
		46	44		
		97	97		
	Verification Sample	12		14	
$[CN]^-$	Calibration Set Only	0	0		R^2=0.996
		83	74		
		150	152		
		275	284		
		292	289		
		472	474		
		738	740		
		1000	996		
#$[Fe(CN)_6]^{3-}$	Calibration Set Only	23	16		R^2=0.999
		55	60		
		280	283		
		499	498		
		1000	1000		

#Concentrations expressed as CN

Table 4 Analysis of a Mixture by Infrared Spectroscopy

Comments	*Actual Concn (mg l^{-1})*		*Concn From Calibn*		*Correlation Coefficient (R^2)*
	CN	*SCN*	*CN*	*SCN*	
	472	253	485	54	
	1000	0	991	0	$R^2 = 0.997$
Calibration	0	100	1	100	(CN)
Set	83	12	121	14	$R^2 = 0.998$
	738	26	742	26	(SCN)
	150	34	103	31	
Verification	292	71	335	67	
Set	275	9	345	8	

Despite the demonstrated capability for detection and speciation of cyanides in solution, the infrared technique appears not be suitable for use as an on-line monitor for effluents. The observed detectable limits are 2-3 orders of magnitude greater than typical discharge limits in effluents (e.g. total cyanide levels in NSW must be below 0.05 mg l^{-1} under current regulations). Sensitivity could only be improved upon by proportionately increasing the pathlength of sample in the measurement cell; however, this would also require the use of a more powerful optical source and/or more sensitive detector. Neither option appears to be readily

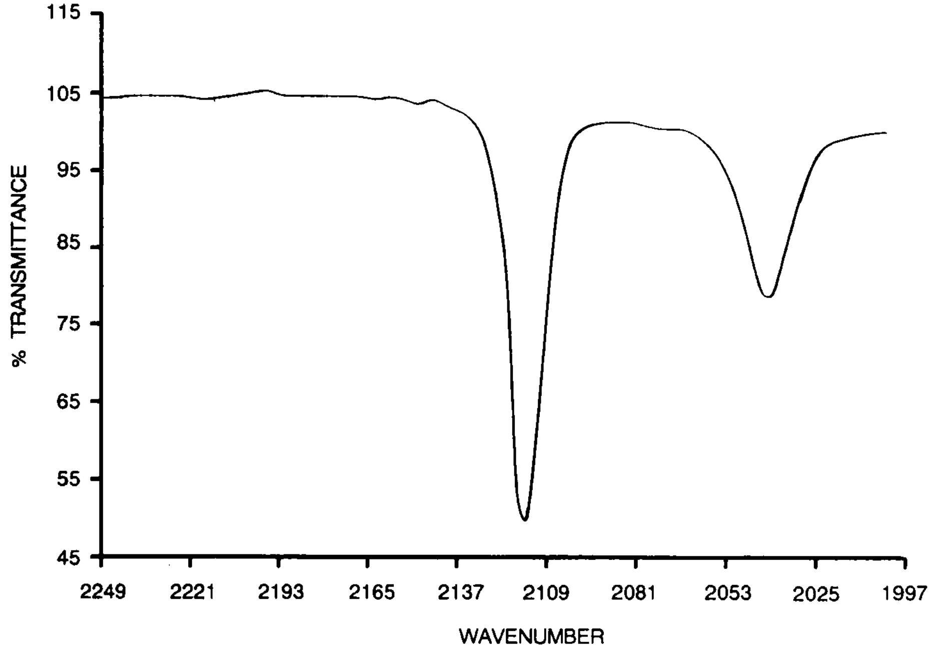

Figure 1 Cyanide stretch region of infrared spectrum of $K_3Fe(CN)_6$

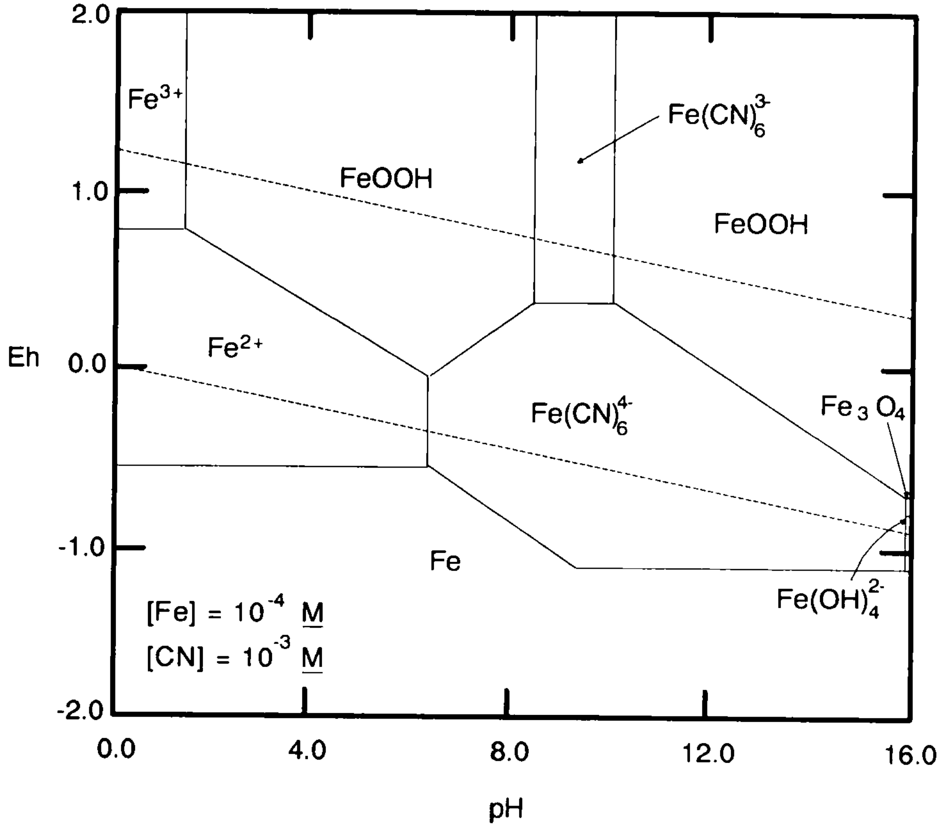

Figure 2 Pourbaix diagram for Fe(II,III)/CN

available. Consequently, it is concluded that IR is not a suitable means of monitoring cyanide species for regulatory compliance. However, in many other applications (e.g. in association with process monitoring and effluent control for gold and electroplating industries) the levels of cyanide species can be several hundred mg l^{-1}, and speciation is an important parameter in the process. In these cases, the potential of the non-invasive infrared technique would be much higher.

Behaviour of Ferricyanide Solutions

Two distinct peaks were present in the CN region of spectra of the sample of potassium ferricyanide, $K_3Fe(CN)_6$; these occurred at 2115 cm^{-1} and 2036 cm^{-1}. The relevant region of the spectrum is show in Figure 1. The peak at 2036 cm^{-1} is not assigned to ferricyanide[7], and it was initially thought that the sample also contained the ferrocyanide ($[Fe(CN)_6]^{4-}$) complex since this had a matching IR band position. However, analysis of a sample by ion chromatography showed only the ferricyanide complex to be present. A solution made up to be 250 mg l^{-1} in $[Fe(CN)_6]^{3-}$) complex analysed as 245 mg l^{-1} by ion chromatography.

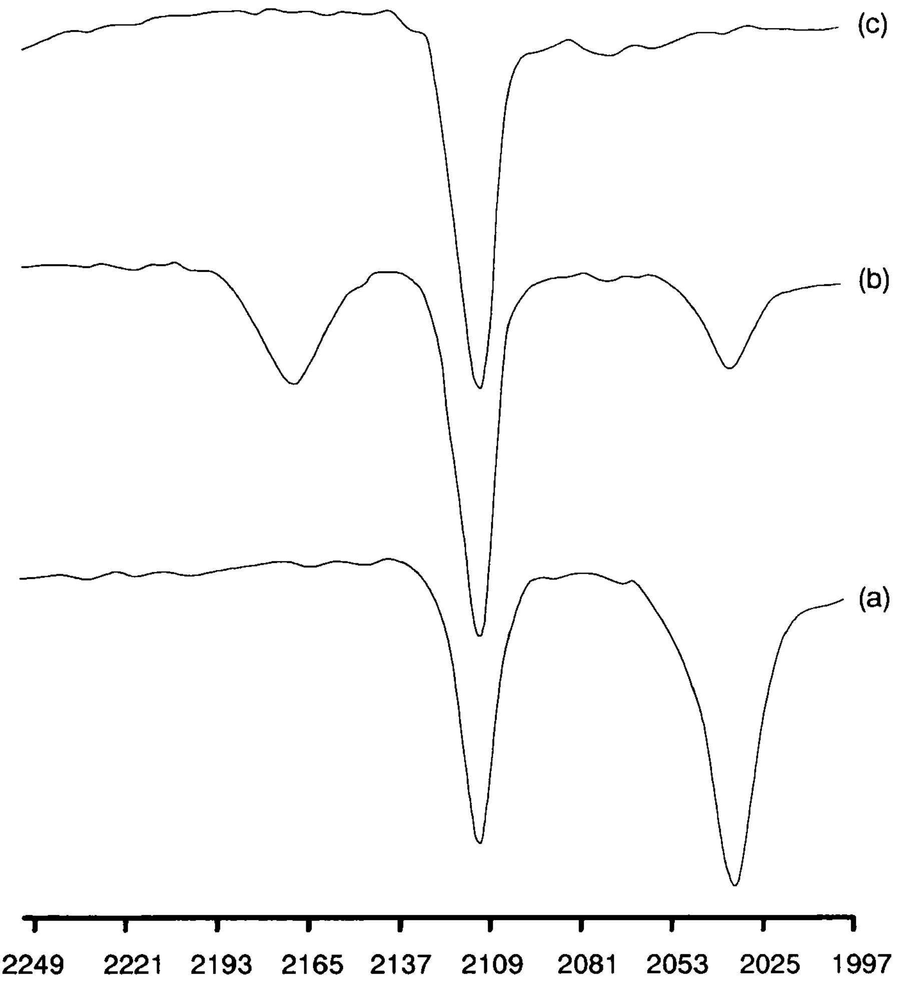

Figure 3 IR spectra of treated $K_3Fe(CN)_6$ solutions: a) original solution b) after exposure to sunlight c) after subsequent acidification

Possibly, the second peak in the ferricyanide spectrum is due to a moderately stable iron aquo-cyano species ($[Fe(H_2O)_x(CN)_6\text{-}x]$) or hydroxo-cyano species ($[Fe(OH)_x(CN)_6\text{-}x]$) formed under the conditions of the solution. As indicated in Figure 2, the ferricyanide complex is expected to be unstable with respect to FeOOH and free cyanide under the high pH (approx 12.5) conditions applying in the solution. The stepwise displacement of CN ligands by H_2O or hydroxide ions would therefore be expected.

If such a ligand displacement was taking place, free cyanide should be formed in the solution. No IR peak due to free CN could be seen; however, the earlier work had established that at low concentrations this peak was very difficult to detect.

Some additional features were noted about the behaviour of the solution under different treatment conditions, in particular, the effects of sunlight, heat, and dilution.

Figure 3 shows the results of a sequence in which the sample was firstly stood in bright

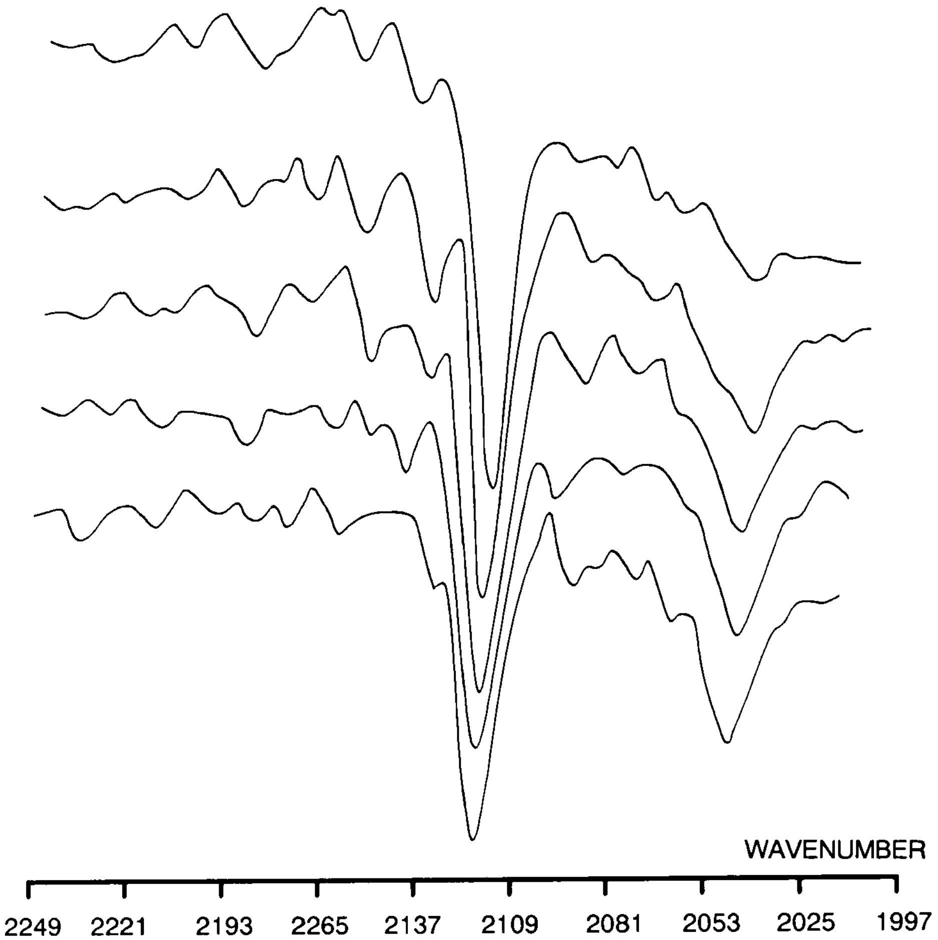

Figure 4 Changes in IR spectrum of $K_3Fe(CN)_6$ solutions with temperature. Uppermost spectrum taken at around 50°C, the subsequent series of spectra were recorded as the solution cooled to room temperature (lowermost spectrum).

sunlight for one hour, and then acidified with H_2SO_4. Some oxidation occurred during the exposure to sunlight; there was a significant decrease in concentration of the second complex (peak at 2036 cm^{-1}), and simultaneously the formation of cyanate (peak at 2168 cm^{-1}). Upon acidification, both these peaks disappeared.

Sunlight (UV light) is a well known means to destroy metal-cyanide complexes[7], and the results of exposure of the sample to light were not unexpected. The more rapid disappearance of the peak at 2036 cm^{-1} is consistent with it being a less stable complex on the path to breakdown to free metal ion. The effects of acidification are also of interest. Cyanate is readily hydrolysed, and its disappearance from the acidified sample was expected. The effects upon the 2036 cm^{-1} complex may provide some evidence that it is a hydroxo-cyano species, as a change in pH would be expected to have a marked effect upon the stability of such a complex.

Next, the effect of temperature was examined. A sample of the $K_3Fe(CN)_6$ solution was heated to around 50°C, placed in the FT-IR spectrometer, and a series of spectra recorded as the solution cooled. The results are shown in Figure 4; at the elevated temperature, the 2036 cm^{-1} complex disappeared from the solution, and reappeared as the solution cooled again. The final spectrum was almost identical to that of the starting solution.

These results strongly suggest that the two species present in solution are in equilibrium, with formation of the ferricyanide ion being favoured at higher temperatures.

A ferricyanide solution, showing the two IR bands, was progressively diluted with 1.0 g l^{-1} KOH solution and a series of IR spectra recorded. The relative proportions of the two CN stretching bands at 2115 cm^{-1} and 2036 cm^{-1} changed with dilution; the 2036 cm^{-1} band eventually becoming the more intense of the two bands. Similarly, the 2036 cm^{-1} band predominated in a very dilute $K_3Fe(CN)_6$ solution, prepared ab initio, and became less intense as the concentration was increased.

This result supports the postulation that the 2036 cm^{-1} band is due to an intermediate aquo-cyano or hydroxo-cyano species. Because the dilution exercise used the same stock KOH solution (1.0 gl^{-1}), the concentration of both KOH and water was unchanged while the concentrations of all other species decreased. This would drive the equilibrium further towards formation of the mixed ligand species, resulting in the observed increase in proportion of the 2036 cm^{-1} band.

CONCLUSIONS

The observed detectable limits in the IR method for the cyanide species studied were 2-3 orders of magnitude greater than typical discharge limits in effluents, and the sensitivity could not easily be improved. Consequently, it is concluded that IR is not a suitable means for monitoring low levels of cyanide species. However, the technique does have moderate sensitivity and is able to perform speciation readily and non-invasively. Since the speciation can be done without disturbing the equilibria between the various cyanide species present in a sample, the technique may have some useful applications in monitoring solutions and effluents with higher levels of cyanide species—such as from the gold and electroplating industries—and also in mechanistic studies; for example, in investigations of reaction kinetics or in studying methods of destroying metal-cyanide complexes.

The presence of a second species occurring in strongly caustic ferricyanide solutions has been noted. Aspects of its chemistry have been recorded, non-quantitatively. Any further studies of this species should attempt to measure the equilibrium constant for its formation and to establish its fate under various conditions. It is possible that ^{13}C NMR spectroscopy could assist in identifying the species: the observed symmetry and the relative intensities of CN peaks would help establish the coordination symmetry about the metal.

References

1. C. Pohlandt, E.A. Jones and A.F.Lee, *J.Sth.Afr.Inst.Mining & Metallurgy*, 11-18 (1983).
2. D.R. Canterford, *Anal. Chem.*, **47**, 88-92 (1975).

3. C. Pohlandt-Watson and M-J. Hemmings, Mintek Report M379, Council for Mineral Technology, Randberg, Sth Africa (1989).
4. D.F. Hilton and P.R. Haddad, *J.Chromatog.*, **361,** 141-150 (1986).
5. R.A. Nyquist and R.O. Kagel, *Infrared Spectra of Inorganic Compounds*, (Academic Press, New York, 1971), 1st ed., 495pp.
6. C.N. Rao, J. Ramachandran and P.S. Shanker, *J.Scientif. & Indust. Research,* **18,** 169-170 (1959).
7. A.G. Sharpe, *The chemistry of cyano complexes of the transition metals*, (Academic Press, London, 1976).