

A critical evaluation of methods applicable to the determination of cyanides

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SYNOPSIS

A literature survey of methods suitable for the determination of cyanides in process streams and effluents is presented. Of the large number of methods published, 92 are examined in detail, emphasis being placed on the selectivity of the methods, i.e. the extent to which they enable one to distinguish between ionic cyanide and metal-cyanide complexes. Methods designed for the determination of 'total cyanide' (i.e. ionic cyanide as well as coordinated cyanide) are evaluated critically. Other aspects of the methods are also considered, such as sensitivity, accuracy, speed, and freedom from interferences.

SAMEVATTING

'n Literatuuroorsig oor metodes wat geskik is vir die bepaling van sianiede in prosesstrome en uitvloeiels word aangebied. Van die groot aantal gepubliseerde metodes, word 92 in besonderhede ondersoek met die klem op die selektiwiteit van die metodes, d.w.s. in watter mate hulle 'n mens in staat stel om tussen ioniese sianied en metaal-sianiedkomplekse te onderskei. Metodes wat ontwerp is vir die bepaling van 'totale sianied' (d.w.s. ioniese sianied en gekoördineerde sianied) word krities geëvalueer. Ander aspekte van die metodes soos sensitiwiteit, akkuraatheid, spoed en afwesigheid van steurings, word ook in oënskou geneem.

Introduction

The accurate determination of cyanides in waste waters and process streams presents difficult analytical problems. In such solutions, depending on the pH value, cyanides occur as molecular acid (HCN), as cyanide ions (CN⁻), and as metal complexes of widely varying stability. Because of the extreme toxicity of hydrogen cyanide and ionic cyanide, accurate and sensitive methods of determination are required for the monitoring of waste water. If the environment is to be protected from pollution, one must ensure that the cyanide content of natural waters does not exceed 0,025 p.p.m. Depending on their stability constant, complexed metal cyanides vary in toxicity. The ionization of such complexes due to changes in pH or to photo-decomposition caused by sunlight can result in the formation of molecular hydrogen cyanide. Even complexes as stable as the cyanoferrates can thus become toxic to marine life, and 0,4 p.p.m. has been determined as the maximum permissible level in fresh waters¹.

In the analysis of waters, ionic cyanide and potentially ionizable metal cyanides are often determined together because of their toxicity. The chlorination of an alkaline solution containing these compounds results in the formation of cyanogen chloride and subsequently, as the result of hydrolysis, harmless cyanate ions. This procedure finds an application in the treatment of industrial waste waters and in analytical procedures for the determination of cyanides. Since only ionizable species are oxidized by chlorine, this method differentiates between the cyanides that are amenable to chlorination and the total cyanide present in a sample². The latter is therefore a measure of the ionizable and non-ionizable cyanide species present. The distillation of two samples is required, one of which will be chlorinated and the other unchlorinated. After distillation, both absorption solu-

tions are analysed for cyanide. The difference in the results obtained is the amount of cyanide amenable to chlorination. For the control of pollution, this differentiation between the cyanides that are amenable to chlorination and the total cyanide present in a sample is generally satisfactory. However, there is no clear-cut division between ionizable and non-ionizable compounds, and the ionization of complex cyanides of, for example, nickel, cobalt, silver, and gold, depends largely on the time, temperature, and amount of chlorine used in the oxidation step.

Frequently, the terms *simple* and *complexed* are used to differentiate between various cyanide compounds. The former term describes cyanides that are readily converted to hydrogen cyanide after acidification to a pH value lower than 4. The term *complexed* is applied to cyanide compounds that require digestion, heating, or other severe methods of decomposition to liberate hydrogen cyanide. This differentiation can be useful with respect to the total cyanide content of a sample; however, it gives little information about the types of species actually present.

In this paper, cyanide compounds are classified as free cyanides (i.e. molecular acid and ionic cyanide) or complexed metal cyanides. The complexed metal cyanides can be further classified as weakly complexed cyanides or as strongly complexed cyanides. (The latter group consists of the very stable hexacyanoferrates and hexacyanocobaltate). The term *total cyanide* is used for all cyanide, i.e. free as well as coordinated cyanide, present in a sample. The concentration of free cyanide in a solution depends on the pH value of the solution and on its content of heavy metals capable of forming cyanide complexes. In alkaline hydroxide solutions (i.e. 0,1 M sodium hydroxide), the free cyanide is completely ionized and stable metal-cyanide complexes are formed. In neutral or acid solutions, the free cyanide is only weakly ionized, and the formation and partial evolution of hydrogen cyanide are favoured. Weakly complexed metal cyanides decompose at pH values lower than 4,

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with the evolution of hydrogen cyanide. Strong metal-cyanide complexes are usually unaffected at room temperature, but partial decomposition can occur with increasing temperature and acid content. Furthermore, the metals released upon decomposition react with undecomposed, strongly complexed metal cyanides to form insoluble heavy-metal double salts, viz $\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$, $\text{KFe}[\text{Fe}(\text{CN})_6]$ or $(\text{UO}_2)_2[\text{Fe}(\text{CN})_6]$. Obviously, a system containing hydrogen cyanide or complexed cyanide precipitates, or both, is unstable, which makes analysis difficult. Sample solutions are stabilized by the addition of sodium hydroxide until the pH value is greater than 11 to prevent losses of volatile hydrogen cyanide. The addition of sodium hydroxide to metal-cyanide precipitates results in decomposition and the formation of metal hydroxides.

In addition to the analysis of process streams and waste waters, it might also be necessary for the cyanide content of the resins and pulps used in a process to be determined. It appears that all complexed metal cyanides are retained on anion-exchange resins from alkaline solution. The acidification of a solution prior to ion exchange would therefore result in decomposition of the weakly complexed cyanides, as described above, whereas strongly complexed metal cyanides, i.e. those of iron (II), iron(III), and cobalt(III), would be expected to be retained on the resin. Also, precipitation might occur within the resin network owing to the reaction between the released heavy-metal ions and the strongly complexed metal cyanides. This reaction might result in the gradual 'poisoning' of the anion-exchange resin, i.e. the resin would lose its efficiency. For effective control of a hydrometallurgical process and accurate determination of the cyanides, the kinds of metal complexes present, as well as their relative stability constants, must be known.

Currently used methods of determination are often slow and subject to interferences. For example, the sensitive pyridine-pyrazolone colorimetric method described by Epstein³, which is also recommended in a modified form in a 'standard' method², requires distillation to separate the cyanide from the interfering substances. The method is time-consuming, does not permit very stable metal-cyanide complexes to be determined, and does not allow cyanide to be quantitatively recovered in concentrations below 0.1 p.p.m.⁴. Similar observations have been made about other methods, and it has been pointed out that, with most of these, ionic cyanide cannot be distinguished quantitatively from metal-cyanide complexes⁵.

It was decided that a comprehensive literature survey should be undertaken, the aim being to select and to recommend procedures for the fast, accurate, and precise analysis of ionic cyanide in the presence of complexed cyanides, and *vice versa*. The study on the determination of complexed cyanides would include the determination of hexacyanoferrates and hexacyanocobaltates, as well as methods that enable one to distinguish between individual metal-cyanide complexes—a further advantage in the control of hydrometallurgical processes.

Decomposition of Complexed Metal Cyanides

Most methods for the determination of the total amount of cyanide present in a sample involve treatment with acid to convert the cyanide species to hydrogen cyanide, followed by distillation. Important aspects of the distillation step are the elimination of interferences and the decomposition of stable metal-cyanide complexes. Among the ions commonly found in waters and effluents, sulphide and thiocyanates are responsible for the most serious interferences.

Sulphide distills with hydrogen cyanide and can have an adverse effect on subsequent methods of determination. Its removal, prior to distillation, involves filtration of the precipitates obtained with cadmium nitrate² or lead carbonate⁶, or by its reduction with sodium hydrogen sulphite⁴. Sulphide can also result from the decomposition of thiocyanate or of thiocyanate complexes when conventional reflux distillation procedures are used. This is particularly the case when a metal salt such as mercuric chloride or cuprous chloride is added as a catalyst to accelerate the decomposition of complexed metal-cyanides⁴. In a 'standard method'², the addition of magnesium chloride instead of cuprous chloride is recommended if the concentration of thiocyanate exceeds 5 mg/l. The relatively harsh conditions required to dissociate complexed metal-cyanides are therefore likely to produce additional interferences.

Current methods of decomposition require boiling under reflux for at least one hour. Although this length of time is generally adequate, the complexes of iron, copper, mercury, and cobalt require longer treatment times because of their stability, and decomposition often does not continue to completion. Procedures that have been developed to cope with the analysis of these complexes involve ligand exchange or irradiation with ultraviolet light to displace the coordinated cyanide. During reflux distillation, ligand exchange by a mixture of two components, 1,2-hydroxy-3,5-benzene disulphonic acid (Tiron) and tetraethylenepentamine (TEP), resulted in the complete recovery of ionic cyanide from Cu^+ , Ni^{2+} , Hg^{2+} , Fe^{2+} , Fe^{3+} , and Cd^{2+} complexes⁷, only cyanide present as hexacyanocobaltate not being recovered. This method is faster than conventional distillation methods. Also, because of the mild conditions employed (a pH value of 4.5 adjusted with hydrochloric acid), many interferences, notably those from sulphide and thiocyanate, are eliminated.

Kruse and Mellon⁸ have reported ligand exchange by the addition of the sodium salt of ethylenediaminetetraacetic acid (EDTA) followed by distillation in the presence of phosphoric acid. Complete recoveries of cyanide ions were obtained from the complexes of iron, copper, nickel, cadmium, chromium, and manganese, and the recovery of cyanide from its cobalt complex was 90 per cent. The cyanide complexes of thallium, silver, and mercury were not considered, and interferences from species other than cyanides were not discussed. This method has the disadvantage that the distillation must be continued until the phosphoric acid is concentrated and becomes syrupy.

More recently, ligand exchange by the addition of

EDTA was advocated for the recovery of cyanide from iron and cobalt complexes^{9,10}. This information is available to the present authors only in abstract form, and no further details are available.

The use of ultraviolet irradiation for the decomposition of metal-cyanide complexes has been investigated^{4,11,12}. The decomposition, even of cobaltcyanides, is achieved in a matter of minutes by irradiation with ultraviolet light, of a sample that has been slightly acidified with phosphoric acid. For ultraviolet irradiation, a mercury lamp of 100 to 400 W and a special quartz cell that can be completely filled with sample solution are required. Because it is rapid, this method lends itself readily to automation⁴. However, ultraviolet irradiation also results in the decomposition of thiocyanate to form sulphide and cyanide, and one must take special precautions to prevent this interference.

Preconcentration of Cyanide Compounds

Since the preconcentration of cyanides by distillation is unsatisfactory in many respects, attempts have been made to use solvent extraction or ion-exchange procedures instead. For example, Wronski¹³ successfully used tributyltin in trichloroethylene to extract and preconcentrate small amounts of ionic cyanide from solutions at pH values from 7 to 10. Cyanide was recovered from the organic phase by the use of a four-stage stripping cycle. This method has the advantage that thiocyanate, complexed metal-cyanides, and sulphide are either not extracted or not stripped. However, it is not clear whether mildly complexed metal-cyanides like $[\text{Zn}(\text{CN})_4]^{2-}$ remain stable under the conditions employed.

A potentially useful method involves the extraction and preconcentration of cyanide compounds by the use of quaternary amines, followed by back-extraction with a sodium hydroxide solution¹⁴.

The concentration of metal-cyanide complexes on a strongly basic ion exchanger, followed by the stepwise elution of pairs of these complexes, has been reported by Burstall *et al.*¹⁵, who found difficulty in eluting several of the adsorbed cyanide complexes. The method is tedious, and requires major changes to make it suitable for analytical purposes.

The adsorption of ionic and some complexed cyanides on a strongly basic ion exchanger followed by the on-column release of hydrocyanic acid with sulphuric acid was employed by Gilath¹⁶, who achieved complete recoveries of cyanide bound to zinc, cadmium, copper, and silver. Although this procedure requires only 20 minutes, it is apparent that the complexes of iron, cobalt, and mercury would resist decomposition, and that incomplete recoveries of cyanide would be obtained in the presence of these metals.

Titrimetric Methods

An excellent review of visual titrimetric methods has been published by Bark and Higson¹⁷. It appears that the earliest method for the determination of cyanide was reported in 1851 by Liebig¹⁸. This method is based on the development of turbidity due to silver cyanide that forms as a result of the reaction between the cyanide

and a silver nitrate solution. A similar method, based on turbidity due to the presence of silver iodide in the presence of ammonia with potassium iodide as the indicator, has been reported by Dénigès¹⁹. Various modifications to these argentometric procedures have been suggested. The American Public Health Association² recommends a modified Liebig¹⁸ method in which p-dimethylbenzylidene rhodanine is used as the indicator²⁰ for the determination of concentrations of cyanide higher than 1 mg/l.

Titrimetric methods involving the electrochemical detection of the end-point are widely used, and are discussed in detail later.

Generally, titrimetric procedures are employed for the determination of larger quantities of cyanide in the absence of weakly complexed metal cyanides and other interferences.

Colorimetric Methods

From the review of methods available for the determination of small amounts of ionic cyanide, it is apparent that colorimetric methods are suitable for amounts such as 0.1 to 1 p.p.m. Few of the methods are specific for cyanide, and there is interference owing to the presence of sulphur, thiocyanate, thiosulphate, and certain metals²¹⁻³⁹.

For the detection and determination of small amounts of cyanide in effluents, Aldridge's method⁴⁰⁻⁴² is recommended. This method is an example of the König synthesis, in which cyanogen bromide or chloride reacts with pyridine and an aromatic amine to form a dye. Aldridge reacted cyanide with an excess of bromine, removing the excess of bromine with arsenous acid solution and allowing the cyanogen bromide to react with a pyridine-benzidine reagent. The König reaction is used in the determination of ionic cyanide. In the presence of thiocyanate, ferrocyanide, and ferricyanide, and sodium and calcium chlorides, a distillation under reduced pressure is recommended after complex cyanides have been 'fixed' with zinc acetate solution^{3,43,44}. However, the use of carcinogenic benzidine is hazardous, and other investigators used a variety of coupling agents^{3,17,21,22,44-51}.

The most successful of these methods is the variation proposed by Epstein³, which involves the oxidation of cyanide to cyanogen chloride with chloramine-T. The cyanogen chloride is then reacted with pyridine containing pyrazolones, and the blue colour produced is measured at 630 nm. This method is sensitive, and can be used in acid, neutral, or slightly alkaline media. A modification of Epstein's method in which a more stable reagent, pyridine-barbituric acid, is employed, is currently recommended by the American Public Health Association².

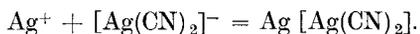
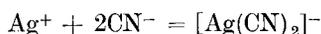
It must be borne in mind that, with methods based on the König synthesis, all ionizable cyanide compounds can be determined, i.e. those amenable to bromination or chlorination. With these methods, one is therefore unable to distinguish between cyanide ions, weakly complexed metal-cyanides, or thiocyanate. To eliminate interferences from compounds other than cyanides, a distillation step prior to colorimetric determinations is recommended. Also, the distillation step must be devised

in such a way that even the most stable cyanide complexes, i.e. those of mercury(II), iron(II), iron(III), and cobalt(III), are dissociated to evolve hydrogen cyanide. Only then does the colorimetric measurement of the ionic cyanide in the absorption solution give an accurate value of the 'total' cyanide present in the sample.

Electrochemical Methods of Determination

Potentiometric Procedures

The potentiometric determination of cyanide with silver nitrate was first reported in 1922, and early procedures up to 1962 have been reviewed by Bark and Higson¹⁷. The most widely used indicator electrode is the silver rod or billet, although gold, mercury, and amalgam electrodes have been used occasionally⁵². The theory of the argentometric titration of cyanide in the absence and presence of ammonia was given by Ricci⁵³. In theory and practice, two points of inflexion are obtained in the potentiometric titration curve, the first being due to the formation of a soluble silver complex, and the second to the appearance of insoluble silver(I) cyanide:



The second inflexion therefore corresponds to the second (permanent) turbidity of the normal Liebig¹⁸ titration and to the end-point given by Dénigès in his modification¹⁹, where ammonia and iodide ions are added as indicator. The change in slope of the first potentiometric inflexion is about ten times greater than that of the second and, because of this and the fact that it is less susceptible to interferences, it is normally used in practical applications. As in the Dénigès titration, the presence of excess ammonia distorts the slope of the second potentiometric inflexion¹⁹ but does not change the first or second equivalence points, since the formation constants of the ammonia complexes of silver are much lower than those of the corresponding cyanide complexes.

When metal ions are added to a cyanide solution, complexes are formed. If the stability constants for these complexes are higher than that for the silver-cyanide complex $[\text{Ag}(\text{CN})_2]^-$, an amount of ionic cyanide proportional to the concentration of metal ions present will be removed from solution, and there will be a reduction in the silver nitrate titre. Under normal analytical conditions, the cyanozincate(II) ion $[\text{Zn}(\text{CN})_4]^{2-}$ reports as ionic cyanide in argentometric titrations. In potentiometric titrations, the equivalence point for zinc cyanide slightly precedes that for $[\text{Ag}(\text{CN})_2]^-$, but zinc concentrations of up to 0.1 g/l can be tolerated before the silver-cyanide complex is distorted during the titration of a 1 per cent solution of sodium cyanide with 1.0 N silver nitrate⁵⁴. In the presence of a complexing agent, the hexacyanoferrate(II) ion gives an inflexion curve that falls between those for silver in argentometric titrations, and does not interfere with the first potentiometric equivalence point⁵⁵. In alkaline⁵² (including ammoniacal⁵⁴) solutions, iron(II)- and iron(III)-cyanide complexes interfere. Under ordinary analytical conditions

in the absence of strong complexing agents, nickel and copper also interfere⁵⁴. Some discrimination against the cyanide complexes of copper can be obtained by use of the second argentometric inflexion point in the presence of sodium thiosulphate⁵⁶.

In addition to silver nitrate, which is more commonly employed, mercuric chloride(I), iodine(I), and nickel(II) ions⁵⁷, and bromine⁵⁸ have been used as titrants for cyanide.

Amperometric Procedures

Amperometric titrations are preferred for low concentrations of cyanide and for automated procedures. The amperometric titration of cyanide is equal in accuracy and precision to the visual Dénigès method, and can be employed for more-dilute samples⁵⁹. Shinozuka and Stock⁶⁰ found that the amperometric titration of cyanide with silver nitrate in 0.1 M sodium hydroxide gave low results, and they substituted 0.1 M sodium sulphite for the sodium hydroxide. For amperometric titrations, rotating or vibrating⁶¹ platinum electrodes are preferred, with dilute silver nitrate solution as the titrant. However, titrations have been done with iodine solution. For the determination of very low concentrations of cyanide, the anodic current that is generated at a polarized silver or gold electrode has been measured direct⁶²⁻⁶⁴. This current is proportional to the cyanide concentration:



The approach has been made the basis of two sophisticated analytical methods involving flow injection^{6,11}.

Polarographic and Voltammetric Procedures

Ionic cyanide depolarizes the dropping mercury electrode to give an anodic wave as follows:

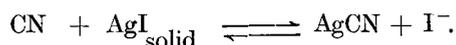


This wave is well developed in 0.1 M sodium hydroxide, and starts at about -0.45 V versus the saturated calomel electrode. Two early procedures^{65,66}, in which simple direct-current (d.c.) polarography was used, were based on this reaction. The advent of sensitive modern waveforms, such as differential-pulse polarography, has permitted the determination⁶⁷ of cyanide in concentrations down to 1.5 $\mu\text{g/l}$. Furthermore, by the use of phase-sensitive, alternating-current (a.c.) polarography and complex-forming electrolytes, metal ions such as chromium, copper, nickel, zinc, cadmium, and iron as well as ionic cyanide, can be determined⁶⁸. An alternative approach for low concentrations of cyanide is the use of anodic-stripping voltammetry, in which the cyanide is deposited as insoluble copper cyanide on the surface of the electrode and subsequently stripped⁶⁹.

Applications Involving Ion-selective Electrodes

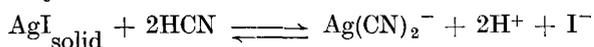
Although these procedures are basically potentiometric, these applications are dealt with separately here because of the different structure of the sensor. Of the halide-membrane electrodes, cyanide-selective membranes based on silver iodide (Corning 476127) or a mixture of silver iodide and silver sulphide (Orion Research 94 - 06) are most commonly used⁷⁰⁻⁸². For both of these,

some form of ion-exchange reaction takes place at the boundary phases of the membrane layer⁷³:



The electrode responds primarily to the liberated iodide ion.

As the electrode responds only to the dissociated ionic cyanide (CN^-), the effect of pH on electrode response can be predicted from a log diagram of the hydrocyanic acid-ionic cyanide dissociation system. Theoretically, the optimum range of pH for the electrode is between 12 and 13, but it can be used at a pH value as low as 7 (provided that the solution is carefully buffered), probably as a result of the reaction⁷⁶



In the presence of metal-cyano complexes, those complexes with a stability constant lower than that of silver (I)-cyanide, e.g. the complexes of zinc and cadmium, also give an electrode response and report as ionic cyanide.

In analytical applications, the cyanide-selective electrode can be used as follows:

- (1) in the direct determination of ionic cyanide in solution, where it gives a true Nernstian response over the concentration range 10^{-1} to 10^{-5} M, or
- (2) as an indicator electrode in the titrimetric determination of cyanide.

Indirect Methods Involving Atomic-Absorption Spectrophotometry

The two general indirect methods for the determination of cyanide involve the following:

- (a) the formation of an insoluble precipitate and the determination of the metal in the precipitate or of the excess metal ion in solution, and
- (b) the formation of a stoichiometric complex, separation of the complex by extraction, and determination of the metal in the complex^{1,83-87}.

Worthy of note with respect to speed, sensitivity, and specificity are the methods described by Jungreis and Ain⁸⁵ and Ramseyer and Janauer¹. The former is specific for ionic cyanide, and is based on the formation of a soluble silver-cyanide complex as a result of contact with metallic silver. The latter is specific for the hexacyanoferrates. Although very sensitive, this method is comparatively slow owing to the separation step involved. Both methods are relatively free from interferences.

Automated Techniques

Automated methods for the determination of cyanides are generally very fast and sensitive.

Flow Analysis

Technicon Auto-Analyzer equipment was used for these analyses^{4,6,11,88}. Often a distillation step is incorporated that not only eliminates interferences but separates the cyanides from particulate matter. The cyanides are determined by colorimetric or amperometric measurement with detection limits that can be as low as 0.5 to

1.0 μg of cyanide per litre. The speed of flow analysis is remarkable and, depending on the conditions employed, sampling rates that vary from 10 to 100 samples per hour can be achieved. Flow analysis differentiates only between simple and complexed cyanides. The term *simple* refers to ionic cyanides as well as to ionizable metal-cyanide complexes that are determined together. The additional determination of strong metal-cyanide complexes can be achieved only by the inclusion of irradiation with ultraviolet light to decompose them.

Gaseous hydrogen cyanide has been separated from other cyanide species by diffusion in Conway micro-diffusion cells prior to flow analysis⁶, but this procedure is extremely time-consuming, taking from 3 to 5 hours⁸⁹.

Gas Chromatography

Nota *et al.*¹² developed a very simple and sensitive method for the determination of trace amounts of iron(II)-, iron(III)-, and cobalt(III)-complexed cyanides. After the complexed cyanides have been broken down by irradiation with ultraviolet light, cyanogen bromide is formed



and is separated by gas chromatography. Ionic cyanide and thiocyanate are converted by hypochlorite into cyanogen chlorides, which are stable under ultraviolet light. Ions commonly found in waste waters (such as Fe^{3+} , Cu^{2+} , and Zn^{2+}) and potential cyanide-forming materials (such as cyanate, glycine, urea, sulphides, and sulphites) do not interfere. The sensitivity is at nanogram level.

Ion Chromatography

This technique⁹⁰ is specific for ionic cyanide, and remarkably free from interferences. It is based on the separation of ionic cyanide from metal-cyanide complexes and other anions, including sulphide and thiocyanate, on pellicular anion-exchange resins. Amperometric measurement after separation allows ionic cyanide to be detected at concentrations of a few micrograms per litre.

Analysis of Solids

The determination of cyanide in solid substances is rarely described in the literature. One method⁹¹, which is applicable to the analysis of stable metal-cyanide complexes, employs fusion with sulphur and a mixture of potassium chloride and potassium carbonate to form thiocyanate. The latter is determined colorimetrically, and the cyanide content calculated. Cyanide is recovered from all metal-cyanide compounds, including the hexacyanoferrates and hexacyanocobaltates.

The method recommended by the American Public Health Association² for the determination of cyanide in solid wastes involves leaching of the sample with distilled water. Insoluble cyanides in a solid sample are determined as usual by distillation. Insoluble iron cyanides can be leached from solid waste by being stirred with caustic soda for 12 to 16 hours.

Discussion and Recommendations

From this survey of 92 potentially useful procedures for the determination of cyanide, it is apparent that most of them are ideally suited to the analysis of samples

containing only ionic cyanide and no interfering substances. The choice of procedure would then depend only on the concentration of cyanide in the sample solution. For example, titrimetric methods are suitable for the determination of concentrations of ionic cyanide above 1 mg/l, procedures involving the use of cyanide-selective electrodes cover the range from 0,05 to 10 mg/l, and with colorimetric methods one is able to detect concentrations as low as 20 $\mu\text{g/l}$.

Unfortunately, unless they are synthetic, samples rarely contain only ionic cyanide. Complex samples, e.g. industrial effluents, contain mixtures of gaseous and ionic cyanide, metal-cyanide complexes of varying stability, and a variety of interfering substances. Irrespective of these, there are very few methods that one can use to distinguish between ionic cyanide and weakly complexed metal-cyanides in such samples. It appears that, for the selective determination of ionic cyanide in the presence of metal-cyanide complexes, the following methods are the most useful with respect to speed, sensitivity, accuracy, and the elimination of interferences:

- (1) an indirect method involving atomic-absorption spectrophotometry, which is based on the formation of $[\text{Ag}(\text{CN})_2]^-$ as the result of contact with silver wire having a large surface area⁸⁵, and
- (2) ion chromatography⁹⁰, based on the separation by ion exchange of ionic cyanide from metal-cyanide complexes and other anions.

None of the methods inspected can be used successfully in the selective determination of cyanide in coordination complexes with metals in the presence of ionic cyanide and other interfering substances. It is therefore common practice for a two-step analytical approach to be used, viz dissociation and separation of all the cyanide species by distillation procedures, followed by determination of the liberated cyanide in an adsorption liquid. The latter step can be carried out by the use of any of the procedures discussed earlier because of the absence of interfering substances. The total amount of cyanide determined minus the amount of ionic cyanide determined by a different method would then give the concentration of cyanide that is complexed with metal ions. However, distillation procedures are unsatisfactory in many respects, as was pointed out earlier.

The most serious interferences are caused by sulphide, thiocyanate, and thiocyanate complexes. It has been shown⁴ that 30 per cent of the thiocyanate present (at the 100 $\mu\text{g/l}$ level) decomposed to cyanide and sulphide when a 'standard' distillation procedure² was used. Sulphide can interfere in subsequent determinations in two ways. Firstly, the detector, for instance a cyanide selective electrode, also responds to sulphide ions, and a positive interference results. Secondly, the sulphide ions are air oxidized to polysulphides that react with the cyanide present to form thiocyanate, which results in a negative interference. The tendency of thiocyanates to decompose during distillation is aggravated by the severe conditions necessary for the decomposition of stable metal-cyanide complexes. For example, the reflux distillation procedure at low pH, which is recommended by the U.S. Environmental Protection Agency (EPA)⁹², has been shown to be

subject to serious interferences from sulphide and thiocyanates⁷. This is also true for the 'standard' method recommended by the American Public Health Association², as was pointed out earlier. It has also been shown that, in the absence of sulphide and thiocyanates, the EPA method gives excellent recoveries of cyanide from all metal complexes except $[\text{Co}(\text{CN})_6]^{3-}$ at concentrations greater than 20 $\mu\text{g/l}$. The method recommended by the American Public Health Association² apparently does not give reliable results at levels around 100 $\mu\text{g/l}$ because there is incomplete absorption of hydrocyanic acid⁴.

The ligand-displacement method of Ingersoll *et al.*⁷ appears to be the only distillation procedure in which no interferences from sulphide and thiocyanates occur. This is achieved by the use of a moderate pH value of 4,5, which allows lead acetate to be added direct into the distillation flask. The lead sulphide precipitate is stable under the conditions chosen, and an excess of lead guards against sulphide that might be generated from the thiocyanate. This procedure gives complete recoveries of cyanide from all metal complexes except $[\text{Co}(\text{CN})_6]^{3-}$ and needs a distillation time of only half-an-hour as compared with at least an hour required by conventional procedures. It is unfortunate that the cyanide cannot be released from the hexacyanocobaltate by use of the distillation procedures discussed here. However, an approximate measurement of the amount of cyanide bound to cobalt can possibly be obtained from determination of the metal by atomic-absorption spectrophotometry.

Distillation methods are relatively time-consuming and inadequate for the routine analysis of large numbers of samples. If a high sampling rate and high sensitivity are required, an automated technique such as flow analysis should be considered. With this type of analysis, concentrations of ionic cyanide of 1 $\mu\text{g/l}$ can be detected, and the total amount of cyanide present in a sample can be determined by the irradiation of metal complexes with ultraviolet light. Irradiation with ultraviolet light is by far the fastest and most effective means of decomposing all metal-cyanide complexes, including $[\text{Co}(\text{CN})_6]^{3-}$. However, thiocyanate is unfortunately also decomposed by ultraviolet light, and gives a positive interference. At present there appears to be no simple solution to the general problem of interference by thiocyanate. In its absence, there should be a decrease in analysis time if irradiation with ultraviolet light is combined with manual distillation procedures. It is also felt that the combination of the ion-chromatography procedure⁹⁰, which was recommended for the determination of ionic cyanide, and irradiation with ultraviolet light could give a fast and sensitive method for the determination of total cyanide.

Methods concerned with the determination of individual metal-cyanide complexes are rare. Usually two or three metal complexes are determined simultaneously as, for example, the hexacyanoferrates⁸⁷. It appears that individual metal-cyanide complexes could be identified by the use of ion-exchange or solvent-extraction separations followed by determination of the metals present by atomic-absorption spectrophotometry.

For the determination of cyanide in solid samples like pulps, the 'standard' procedure discussed earlier can be used. The analysis of resins should follow similar lines, i.e. leaching with water or sodium hydroxide solution for free and simple cyanides, and distillation procedures (possibly in the presence of EDTA) for complexed metal-cyanides. It appears that analysis involving resins requires moderate sequestering agents so that interferences from the decomposition of the resin itself can be avoided.

Conclusions

It appears that most titrimetric, colorimetric, and electrochemical methods (including potentiometry and the use of cyanide-selective electrodes) for the determination of ionic cyanide are liable to interference from ionizable metal-cyanide complexes, e.g. $[\text{Zn}(\text{CN})_4]^{2-}$. These methods can therefore be employed only if such complexes are known to be absent. Potentially accurate methods for the determination of ionic cyanide include ion chromatography (because of its ability to effect separations) and indirect atomic-absorption spectrophotometry based on the selective formation of $[\text{Ag}(\text{CN})_2]^-$.

Similarly, none of the methods mentioned gives a reliable result for the 'total' amount of cyanide present in a sample. The decomposition of stable complexes and the separation from interfering substances by distillation is therefore necessary. However, most distillation procedures cannot effect the decomposition of all the metal-cyanide complexes, and they suffer from interferences. The most useful distillation procedure appears to be the ligand-displacement technique of Ingersoll *et al.*⁷. With this method, interference from sulphide and thiocyanate can be avoided, and all the ionic and coordinated cyanide — except cyanide from $[\text{Co}(\text{CN})_6]^{3-}$ — present in a sample can be distilled out.

Because of its speed in decomposing cyanide complexes, irradiation with ultraviolet light warrants further attention. A combination of this method with the separation, by ion chromatography, of interfering species might result in a fast method for the determination of total cyanide.

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An international conference on Mines Transport will be held in Stanhope Bretby, England, from 27th June to 2nd July, 1983. An exhibition of related British equipment will be staged in Swadlincote (five minutes distance from Bretby).

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Those interested to have further information should contact Richard West, ABMEC '83 Conference and Exhibition, Mining Industry Promotions Ltd, P.O. Box 53, Rickmansworth, Herts, WD3 2AG, U.K. Tel: 0923 778311, Telex: 296689 WESTEX G.

Analytical chemistry

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Further details are obtainable from Miss P. E. Hutchinson, Secretary of the Analytical Division, Royal Society of Chemistry, Burlington House, London W1V 0BN, U.K.