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ASPECTS  
OF  
CYANIDE ANALYSIS.

by

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## INTRODUCTION

Our work at the Wastewater Technology Centre, Burlington, has included analyses of samples from cyanide removal processes on waste streams from blast furnace plants and gold mining operations. These analyses have included requests for free, simple, complex and total cyanide, cyanate and thiocyanate.

This presentation takes into account some of the problems we have encountered and the approaches we have taken to cyanide analysis. The information is not new and should not be considered definitive, but hopefully will be of some help in the discussion of the Gold Processors Work Group.

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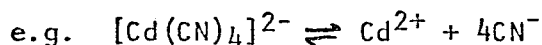
## 2 DEFINITIONS

### 2.1 Free Cyanide

This term includes hydrogen cyanide gas and non-complexed cyanide ions (CN<sup>-</sup>). The relationship between the two is obviously pH independent.

### 2.2 Simple Cyanides or Weak Cyanide Complexes

These are cyanides that could be described as those metallic complexes of cyanide which have relatively high stability constants (pK > 20): Examples of these are the metallocyano complexes of cadmium, zinc and manganese. When these materials are dissolved in water and the pH is adjusted to 12, they split into their constituent parts.

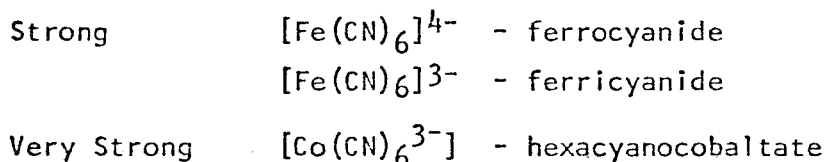


### 2.3 Medium Strength Cyanides

These complexes only split partially into their constituent parts when treated as in above paragraph. An example of this type of complex is the tetra cyanonickelate ion [Ni(CN)<sub>4</sub>]<sup>-2</sup>.

### 2.4 Strong and Very Strong Cyanide Complexes

These complexes require very rigorous procedures for decomposition. The procedures are usually strong acid digestions or ultra-violet irradiations. Examples of these complexes are:



### 2.5 Thiocyanate

This is an ion which might possibly be re-named as sulphocyanide ion because in reality it is also a complex cyanide. Models

### 3 MEASUREMENT OF CYANIDE AND ITS COMPLEXES

#### 3.1 Free Cyanide

Generally, this is not a parameter for which analysis is required. However, an approach to the analysis of hydrogen cyanide was outlined by Montgomery, Gardiner and Gregory<sup>6</sup>. In the method (designed for field use on river samples), the hydrogen cyanide present is extracted by equilibrating the sample with 1,1,1-trichloroethane. The extracted hydrogen cyanide is then transferred into sodium pyrophosphate solution and the determination is completed colorimetrically<sup>7</sup>. According to Montgomery et al, there are no serious interferences. The main considerations would be the effectiveness of the extraction of the hydrogen cyanide, and the pH changes effected when the HCN is extracted.

#### 3.2 Simple Cyanides (pK < 20)

The analytical approaches described here would also take into account those cyanides defined as "free".

The first approach, suitable for levels of about  $10^{-6}M$ - $10^{-4}M$  or 0.026 to 2.6 mg/l  $CN^-$  is described by Serkerka and Lechner and was designed for relatively clean samples such as effluents. We have experienced difficulties when trying to use the method on in-plant samples. An Orion specific ion electrode is used to measure cyanide ion activity and this requires that iodide and sulphide ions be absent. Iodide behaves as a positive interference and sulphide literally poisons the electrode surface. The importance of pH control, procedures for polishing the electrode, and sulphide removal techniques are described. By controlling sample pH very exactly, greater sensitivity can be achieved. By polishing the electrode surface, better responses are possible. By using bismuth nitrate for sulphide removal, relatively fast and permanent sulphide precipitation is effected.

Another approach is the standard silver nitrate titration, although this procedure should not be used without a knowledge of the possible interferences in the sample. Arsenate, thiocyanate, halides, sulphides and thiosulphate can all react with silver ion and

should be removed or accounted for. Although there are several suitable indicators for end point detection in this titration, we are currently investigating the use of a sulphide specific ion electrode. The electrode detects excess silver ion after the cyanide is used up and when coupled to a millivolt meter this results in a large easily detectable change in potential.

### 3.3 Total Cyanides

#### 3.3.1 Sample pretreatment

Because of the presence of complex cyanides, oxidizing agents, sulphides, thiocyanates, cyanates, and other interfering species, the first step in any method of total cyanide determination is sample pretreatment. There are several pretreatment methods available which break down cyanide complexes and either separate or decompose interfering species.

- (i) vacuum distillation of the sample in the presence of sulphuric acid and metal salts<sup>10</sup>,
- (ii) vacuum distillation of the sample in the presence of sulphuric acid and cuprous chloride<sup>11</sup>,
- (iii) vacuum distillation of the sample in the presence of hydrochloric acid alone<sup>12</sup>,
- (iv) vacuum distillation in the presence of hydrochloric acid and sodium arsenite<sup>13</sup>,
- (v) ultra-violet irradiation<sup>15</sup>.

Our experience with these distillations indicates that of the first four, the fourth is the easiest and gives good recovery of all levels of cyanide from 0.01 ppm to 1000 ppm. We have checked the system using sodium cyanide and some soluble complex cyanides of nickel, iron, and copper. This technique does not break down the very strong complexes of cobalt and gold. We are also unsure of the recovery of precipitated ferrocyanides [iron(III) ferrocyanide and copper (II) ferrocyanide].

The last of these procedures (the ultra-violet irradiation) will decompose the cobalt and gold complexes; however, it also partially

decomposes thiocyanate ions into cyanide and one or more of elemental sulphur, sulphate or sulphide<sup>15</sup>.

### 3.3.2 Measurement after sample pretreatment

3.3.2.1 Non-colorimetric methods. The earliest reported method for determining cyanide ion in the sodium hydroxide absorbing solution is Liebig's titrimetric method based on the formation of turbidity due to silver cyanide after all the cyanide has reacted with standard silver nitrate solution. There are several methods for detecting excess silver ion, including the potassium iodide indicator (20 to 10,000 ppm CN), p-dimethylaminobenzalrhodanine indicator (5 to 20 ppm CN), and the sulphide electrode to detect the excess of silver.

### 3.3.2.2 Colorimetric methods.

(i) Method involving formation of a metal complex. A method which is currently being used at the Vancouver laboratory of E.P.S.<sup>18</sup>, is based on the colored complex which is formed when hydrogen cyanide is absorbed in an ammoniacal nickel solution forming nickel tetracyano-dianion.

(ii) Methods based on the modified Konig reactions. In the detection and determination of small amounts of cyanide ion, some reactions are based on the oxidation of cyanide ion to a cyanogen halide (CNX) in which  $CN^+$  is the reactive species. The  $CN^+$  reacts with pyridine and another material present together in a mixed reagent to form a colored complex. Usually chloramine T is used to oxidize the cyanide ion to cyanogen chloride. There have been several "mixed reagents" used in this colorimetric measurement. These two are:

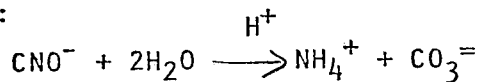
- a) pyridine-barbituric acid - Murty et al<sup>19</sup>.
- b) pyridine-pyrazolone - Epstein<sup>20</sup>.

(iii) Other colorimetric tests. The use of picric acid<sup>21</sup> involves simple procedures, easily prepared reagents and a stable developed colour. The procedure is good to use on a pre-treated sample (distilled under vacuum). However, when attempting to use it on an untreated sample, several points must be remembered. Iron complex cyanides are not measured by the technique. Other interferences include sulphide and sulphite.



(iv) Cyanate. The analysis of this ion is of importance when evaluating the effectiveness of various oxidizing agents on cyanide and its complexes.

The most practical means of analysis of this parameter is the measurement of ammonia produced when the cyanate ion is heated near the boiling point for several minutes. The quantitative reaction which occurs is:



Several well-known, reliable methods for ammonium analysis can be utilized. We have found the Orion specific ion electrode to be most satisfactory for these samples.

(v) Thiocyanate. The red colour intensity developed when a solution of a ferric salt is added to a solution containing thiocyanate obeys Beer's law. The test has relatively few interferences. Substances which do interfere are mercuric salts and oxalic acid. These materials suppress the reaction. Sulphide ions produce a colloidal precipitate but can be removed by treating the sample with lead carbonate and filtering off the precipitate. This test is discussed more fully in "The Analysis of Raw, Potable, and Waste Waters"<sup>14</sup>.

Fe<sup>+++</sup>  
SCN<sup>⊖</sup>

4. RECOMMENDATIONS

1. The picric acid test should not be used directly on samples known to contain iron complex cyanides or sulphides.
2. Thiocyanate should be considered a complex cyanide. It can either be measured separately as thiocyanate or as a cyanide<sup>15</sup>. Some further work would have to be done with the UV irradiation technique to quantitate the breakdown of thiocyanate.
3. In the measurement of total cyanide, the hydrochloric acid-sodium arsenite pretreatment should be considered to include soluble complex cyanides excluding cobalt, gold and thiocyanate. The other acid distillations mentioned are similar.
4. There are no easy ways of measuring simple cyanides in waste samples other than effluents. Since the direct silver nitrate titration may be of questionable value on these samples, further work should be carried out.
5. Thus, when a cyanide value is reported, perhaps a reference to the method used should be included.

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