



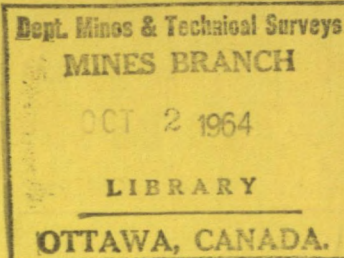
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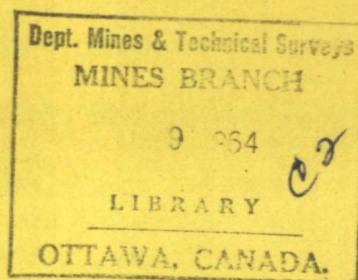
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R 127

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MEASUREMENT OF FREE CYANIDE
CONCENTRATION BY CONTINUOUS
POTENTIOMETRIC TITRATION



J. C. INGLES

EXTRACTION METALLURGY DIVISION

JULY 1964

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MEASUREMENT OF FREE CYANIDE CONCENTRATION
BY CONTINUOUS POTENTIOMETRIC TITRATION

by

J. C. Ingles *

ABSTRACT

The use of commercially-available precision metering pumps makes possible the continuous argentometric titration of free cyanide in process solutions. End-point indication, provided by continuous measurement of the potential of a silver wire-reference electrode combination, gives a good approximation of the actual cyanide content of the samples and, further, is ideally suited to automatic control of cyanide addition to the process. The response time is of the order of 2 minutes, but could be reduced. The procedure requires a clarified solution and is not applicable to unfiltered ore pulps or slurries.

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Appendix: Theoretical Basis of the End-point Detection System. 18-20

Chet, Section de chimie analytique, Division de la métallurgie extractive, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

Direction des mines

Rapport de recherche R 127

MESURE DE LA CONCENTRATION EN CYANURE LIBRE
PAR TITRAGE POTENTIOMÉTRIQUE CONTINU

par

J. C. Ingles*

RÉSUMÉ

L'emploi de pompes à mesurer de précision, disponibles dans le commerce, a permis de faire le titrage argentométrique continu du cyanure libre dans les solutions de traitement. L'indication de virage fourni par la mesure continue du potentiel de la combinaison d'un fil d'argent et d'une électrode de référence donne une bonne estimation de la teneur réelle des échantillons en cyanure et, de plus, convient parfaitement au contrôle automatique de l'addition de cyanure lors du traitement. Le temps de réponse est de l'ordre de 2 minutes, mais peut être réduit. Le procédé exige une solution clarifiée et ne peut servir si l'on a affaire à des pulpes ou des boues de minerai non filtrées.

*Chef, Section de chimie analytique, Division de la métallurgie extractive, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

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INTRODUCTION

The successful application of continuous measurement and control of alkalinity to gold ore cyanidation circuits, which has given significant improvements in gold extraction and reagent economy (1), has suggested that even greater benefits might be derived from continuous measurement of free cyanide concentration. The apparatus employed for this purpose should be simple, rugged, and unaffected by vibration, if it is to be applied in a gold mill. It would, of course, be preferable to perform the measurement directly in the leach pulp; but, in any case, the response time (the interval from the time the solution enters the apparatus until the measurement is recorded) should be minimal.

The literature contains several references to methods for the continuous measurement of cyanide concentration in gases or solutions, and other references describe reactions which could be automated for this purpose. These include applications of polarographic (2)(3), potentiometric (4)(5), amperometric (6), and colorimetric (7) methods. A coulometric procedure has been proposed for the continuous determinations of halogens, using electrically-generated silver ions (8), and appears to be equally applicable to cyanide determination.

The recent availability of highly-precise metering pumps (e. g. Beckman catalogue Nos. 74600-74603) has introduced the possibility of carrying out continuous titrations in which accurately-metered sample and reagent streams can be blended and in which some property of the system characteristic of the end-point can be monitored in the reaction mixture. The precision and reliability of the well-known Liebig argentometric method for free cyanide seemed suitable to this approach, with appropriate modification, and this combination was therefore investigated.

This report, then, describes (1) the construction of an apparatus for continuously (and virtually instantaneously) titrating the free cyanide content of a cyanide leach solution, (2) the formulation of a suitable titrating reagent for use in this titration, and (3) the development of a potentiometric end-point system which not only provides an indication of whether the solution being analyzed has the desired concentration of free cyanide, but permits the measurement and recording both of the direction in which the solution deviates from the desired value and of the amount of this deviation.

Since the work described here was completed, a report on an extensive study of the use of these same metering pumps for continuous

titrations has appeared (9). In it, however, neither the application to free cyanide titrations, nor the possibility of quantitative interpretation of the electrode response, is mentioned.

EXPERIMENTAL

The development of the equipment described herein hinged principally on the properties of the titrating solution to be used with it. The factors involved in the formulation of this reagent are thus of primary importance, and it is necessary to deal with them before proceeding to a description of the construction of the apparatus itself.

Choice of Reagent Composition

It is not desirable to use the simple silver nitrate solution of the original Liebig method in this application, for two reasons: First, if silver ion is in sufficient excess (that is, if the cyanide concentration of the entering sample solution is low), the precipitating silver argentocyanide will coat the interior of the measuring chamber and cause erratic operation by redissolving whenever higher cyanide concentrations are encountered. Secondly, because of this precipitation the titration curve will not be symmetrical so that it would not be possible to estimate the cyanide concentration of a solution in which the cyanide concentration was less than the concentration equivalent to the reagent solution being used.

Precipitation of silver argentocyanide is overcome, in the Dénigès modification of the Liebig method, by adding ammonia to the sample solution. The presence of ammonia also makes available, for quantitative interpretation, the half of the titration curve that is normally cut off as a result of the precipitation. Since the ammonia addition would normally require addition of an extra pump to the apparatus, the possibility of combining the ammonia in the reagent was investigated in preliminary experiments.

Another factor of importance in establishing a suitable reagent composition is related to the requirements of the end-point detection system. In the course of preliminary work leading to the procedure described herein, the silver metal-argentocyanide ion combination, used as an electrode of the second type for cyanide, was investigated and was shown to provide a convenient method for measuring the cyanide-ion activity of pure cyanide and of cyanide-cuprocyanide mixtures. The theoretical considerations that form the basis for interpreting the response of this electrode system in terms of cyanide ion activity are discussed in an appendix to this report (pp. 19-21). As indicated in that discussion, the presence of argentocyanide

ion at a sufficiently high concentration should make it possible to interpret quantitatively the silver electrode potential, before and after the inflection point, in terms of cyanide ion concentration.

After a number of preliminary experiments, a reagent solution was formulated on the basis of the above considerations. This reagent solution contained a sufficient concentration of free silver ion that when pumped at a convenient volume ratio with respect to a sample solution containing the desired free cyanide concentration, the two solutions would be equivalent and the electrode system would indicate an EMF corresponding to the stoichiometric end-point.

To establish that EMF measurements above and below the stoichiometric end-point could, as predicted by the discussion in the appendix, be interpreted quantitatively, a series of measurements was carried out on solutions of known free cyanide concentration. The actual experiment was performed using the Precision-Dow Titrometer (a recording potentiometer-titrator) to pump a cyanide solution of known concentration into a measured aliquot of the reagent solution. A number of silver electrode-reference electrode combinations were used, and the EMFs were recorded on the Titrometer chart as a function of the volume of cyanide added. In this way, the Titrometer provided a rapid, convenient method for carrying out and recording a continuous series of such measurements automatically. Figure 1 illustrates one such chart recording. In Figure 2 the cyanide concentration, in excess or deficit with respect to the equivalence point, has been calculated from this recording and is plotted on ascending (right-hand side) and descending (left-hand side) logarithmic scales. The ordinates, plotted on a linear scale, represent the corresponding increase (right-hand side) and decrease (left-hand side) from the value of the EMF corresponding to the stoichiometric equivalence point or control value*. The results of a number of such experiments showed that the solution formulation adopted could be depended on to give reproducible, quantitative values for the free cyanide content of the sample solution titrated with it. The high degree of symmetry of these curves, and the close approach to the theoretical slope for the overall 2-electron reaction as discussed in the appendix, can also be noted from these two figures.

The reagent solution that was finally adopted for the work described herein was 0.001M in free silver ions, 0.01M in sodium argentocyanide, 0.02M in sodium hydroxide, and 0.05M in ammonia. It appears to be stable almost indefinitely in glass. There is a slight reaction with the

*The control value is the term used here to describe the free cyanide concentration at which it would be desired to maintain the sample solution in a mill application.

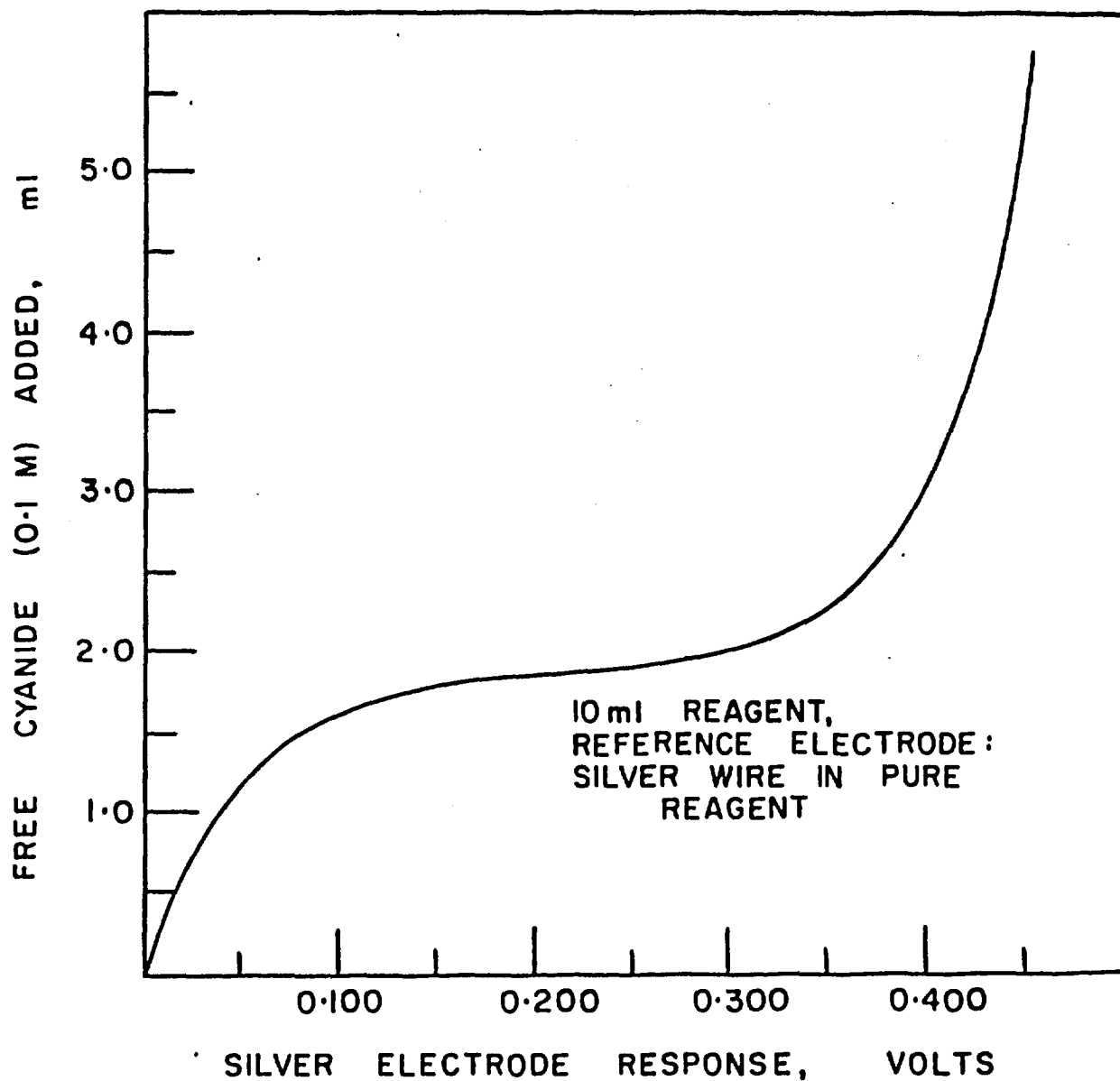


Figure 1. Chart recording of EMF measurements on the reagent solution as a function of free cyanide added.

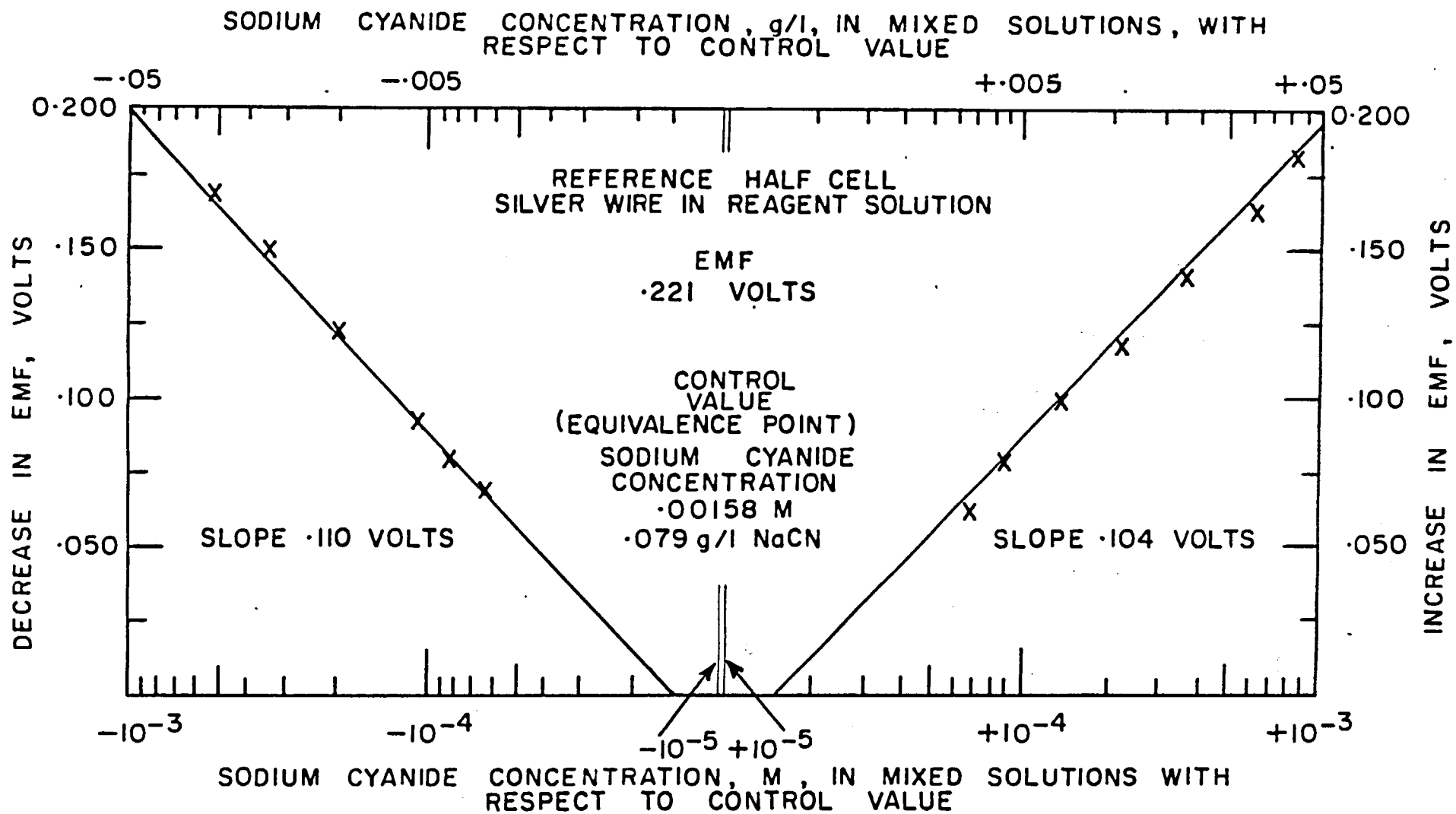


Figure 2. Silver electrode response on either side of control value, using reagent solution with added silver and ammonia.

plasticizer in laboratory vinyl plastic tubing, but the flocculent, pale-brown precipitate which forms in the tubing has not created any difficulties. The free silver content can be adjusted to permit control at almost any cyanide concentration desired.

Other Reagents

Stock cyanide solution: A solution of sodium cyanide, in air-free water at pH 12, was adjusted to a concentration of 5 g NaCN per litre. It was freshly diluted with water at pH 12 to give the concentration desired for each series of tests.

Design of Apparatus

The set-up finally adopted is shown diagrammatically in Figure 3, and Figure 4 is a photograph of the actual apparatus. Figure 5, a block diagram, shows the suggested method of sampling, and the manner in which the analyzer could be used for control of a cyanide mill circuit. The components are: the two metering pumps, whose precision is the main factor in making the method possible; the mixing section; and the measuring section.

The chief design consideration in assembling the apparatus is to make the response as rapid as possible. To accomplish this, it is necessary to keep the internal volume, from the point where the sample solution enters the analyzer to the point where the mixed solution enters the measuring section, at a minimum with respect to the sample metering rate. This can be controlled partly by the layout of the tubing. The use of air for mixing helps fill free space beyond the mixing point, further reducing hold-up of solution. Carrying the clarified solution from the sampling point in the process to the apparatus by means of a high-speed auxiliary pump is, of course, essential. The remaining factor is hold-up in the sample metering pump itself. A 5-ml Beckman metering pump was chosen for the bench-scale apparatus described here, to avoid consuming the sample too rapidly. This particular pump may not be the best choice from the point of view of prompt response, however, because of its internal volume/pump rate ratio, which limits overall response to about 2 minutes. The higher-capacity pump used for reagent metering has a more favourable ratio and its use for sample metering, which would be practical in a mill circuit, should result in a significantly faster response.

Electrodes

The indicating electrode is a plain coil of 18-gauge silver wire, and requires no special preparation. A similar coil, dipping into a portion of the pure reagent solution contained in a glass shell of the type used for the usual commercial calomel reference electrode--in this case,

MIXING AND AIR SEPARATION SECTION

MEASURING SECTION

DETAIL OF REFERENCE ELECTRODE

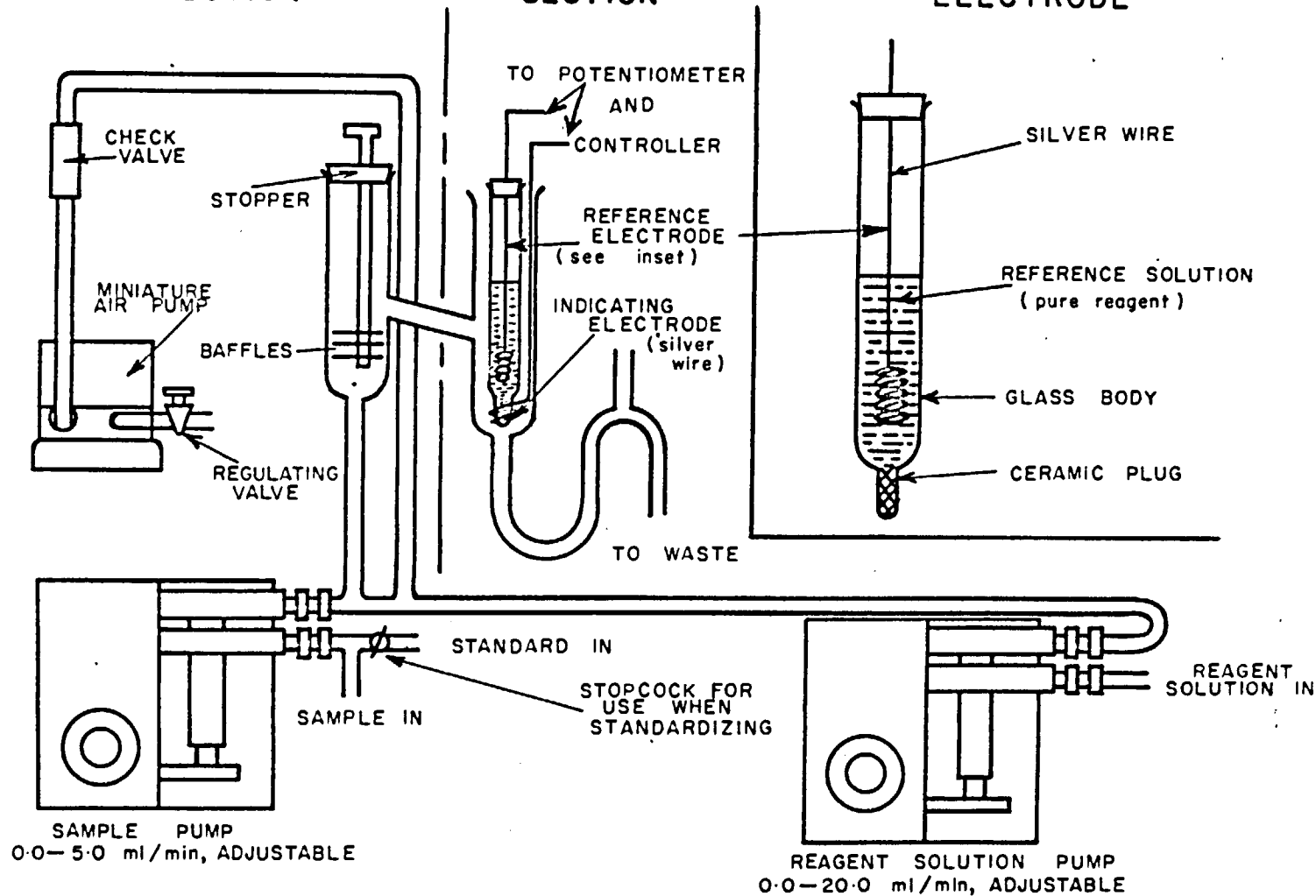


Figure 3. The set-up of the continuous cyanide solution analyzer.

plasticizer in laboratory vinyl plastic tubing, but the flocculent, pale-brown precipitate which forms in the tubing has not created any difficulties. The free cyanide concentration can be adjusted to permit control at almost any cyanide concentration.

Other

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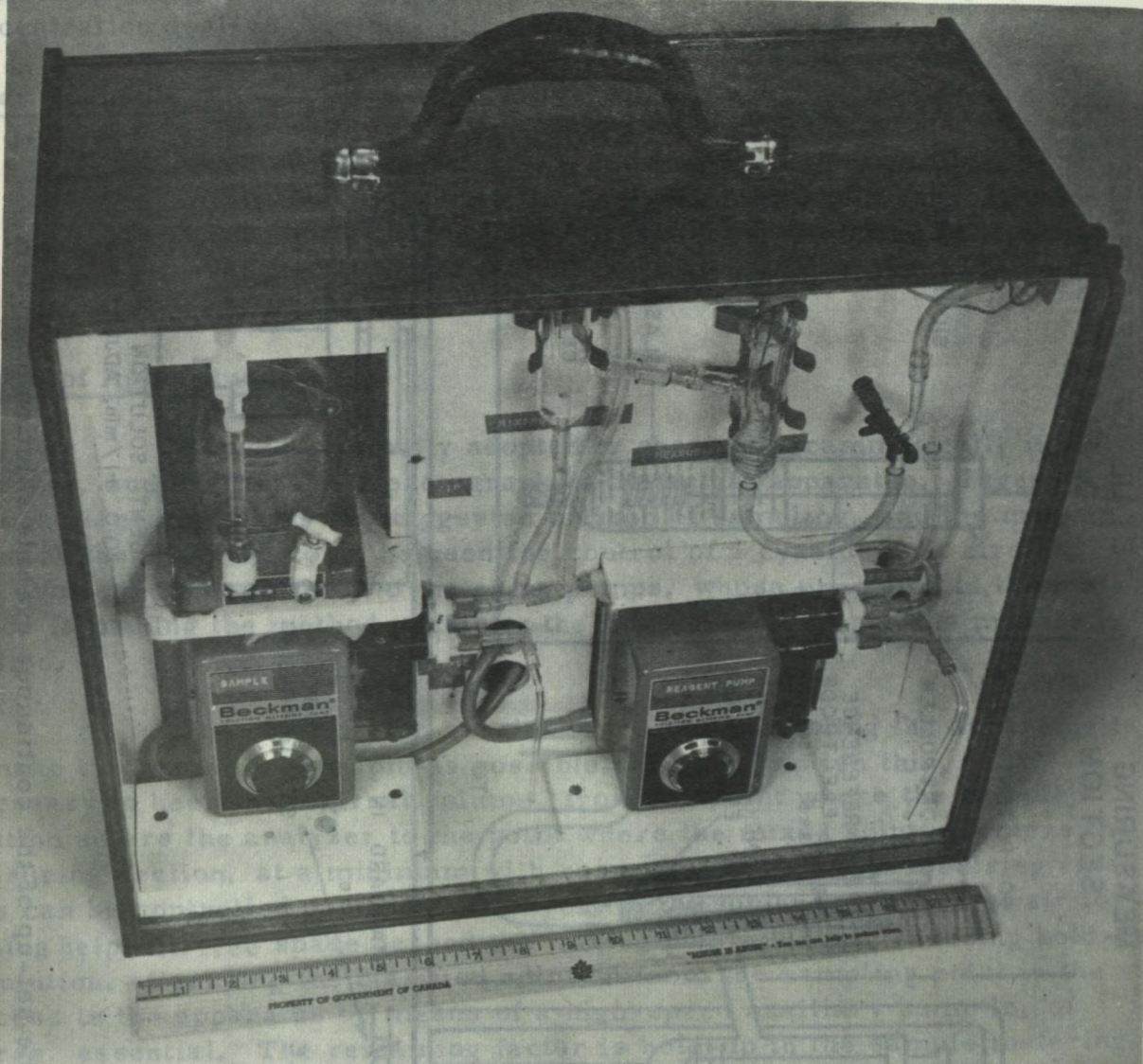
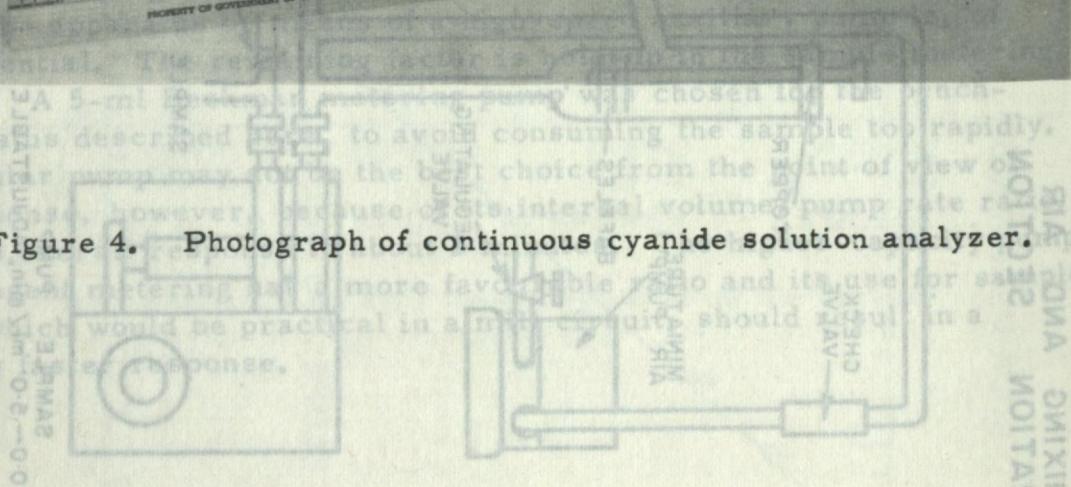


Figure 4. Photograph of continuous cyanide solution analyzer.



The indicating electrode is a plain coil of 18-gauge silver wire, and requires no special preparation. A similar coil, dipping into a portion of the pure reagent solution contained in a glass shell of the type used for the usual commercial calomel reference electrode--in this case,

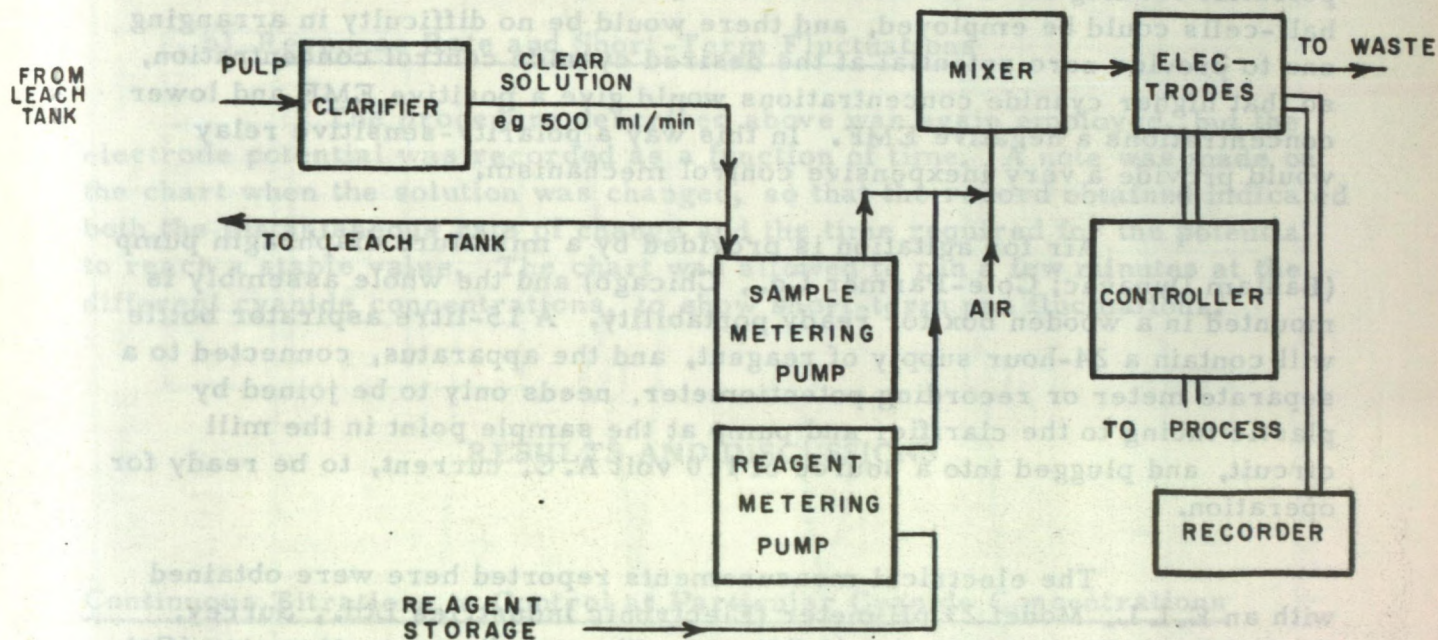


Figure 5. Block diagram showing suggested method of sampling, and use of analyzer for control of a cyanide circuit.

the shell from the Electronic Industries RJ 23 electrode, which has a porous ceramic plug as a bridge--serves as a reference half-cell. This shell will retain the reference solution for over a week. It would be a simple matter, however, to lead the reagent solution through the reference electrode shell on its way to the mixing point, to ensure that the half-cell always remained full.

Use of the reagent as the reference solution ensures a zero potential reading for a solution containing no cyanide. Other reference half-cells could be employed, and there would be no difficulty in arranging one to provide zero potential at the desired cyanide control concentration, so that higher cyanide concentrations would give a positive EMF and lower concentrations a negative EMF. In this way a polarity-sensitive relay would provide a very inexpensive control mechanism.

Air for agitation is provided by a miniature diaphragm pump (Bantam Dynavac; Cole-Parmer Co., Chicago) and the whole assembly is mounted in a wooden box for ready portability. A 15-litre aspirator bottle will contain a 24-hour supply of reagent, and the apparatus, connected to a separate meter or recording potentiometer, needs only to be joined by plastic tubing to the clarifier and pump at the sample point in the mill circuit, and plugged into a source of 110 volt A. C. current, to be ready for operation.

The electrical measurements reported here were obtained with an E. I. L. Model 23 pH meter (Electronic Industries Ltd., Surrey, England). A Photovolt Model 43 "Varicord" recording potentiometer (Cat. No. 7599, Photovolt Corp., New York) was used to obtain response-rate curves and to demonstrate application of the equipment to continuous recording. A lamp-photocell combination actuated by a shutter mounted on the pen carriage, and operating a relay, was used to demonstrate the control possibilities of the set-up.

Procedure

a) Continuous Titrations to Control at Particular Cyanide Concentrations

The apparatus was assembled as already described, and a short glass inlet tube was provided at the sample metering pump to permit feeding from a beaker. Fresh cyanide solutions covering the desired ranges were prepared, as required, by diluting the stock cyanide solution with water of pH 12. Burettes were used for dispensing these solutions to ensure accurate dilution. The apparatus was started and the metering rates of the sample and reagent pumps were adjusted to the desired values by means of the calibrated dials. The inlet tube was then immersed in a beaker containing one of the standard cyanide solutions and after 5 minutes the electrode potential was read. Following this, the beaker was replaced with the next standard and

another measurement made. This was continued until the desired concentration range had been covered. Then the metering rates of the two pumps were changed to provide a different flow-rate ratio, and the process was repeated. The approximate settings needed to give the maximum change of potential (end-point or control-point response) for a particular cyanide concentration could be estimated from a direct titration of the sample with the reagent, using either a visual (chemical) indicator or a potentiometer. Alternatively, a more satisfactory estimate could be obtained for all other settings after the curve for any particular pair of settings had been plotted.

b) Response Rate and Short-Term Fluctuations

The procedure described above was again employed, but the electrode potential was recorded as a function of time. A note was made on the chart when the solution was changed, so that the record obtained indicated both the instantaneous rate of change and the time required for the potential to reach a stable value. The chart was allowed to run a few minutes at the different cyanide concentrations, to show short-term pen fluctuations.

RESULTS AND DISCUSSIONS

Continuous Titrations to Control at Particular Cyanide Concentrations

Figure 6 shows typical calibration curves for the three pairs of metering-pump settings that would be used for controlling at 0.50, 1.0 and 1.5 grams of NaCN per litre, respectively. For comparison, Figure 7 shows the calibration curves calculated on the basis of a direct potentiometric titration of the reagent with a standard cyanide solution using the Precision-Dow Titrometer. The shapes of the curves obtained experimentally coincide reasonably well with those of the calculated curves, but there is a significant difference between the calculated pump settings and those actually used to obtain the experimental curves. This difference indicates that the actual volumes metered by the pumps differ from the dial calibrations. Such a deviation can be corrected, and is not significant in relation to the applicability of the method. Reproducibility, on the other hand, which is a much more important factor, is excellent. Curves prepared months apart match very closely.

Response Rate and Short-Term Fluctuations

Figures 8 and 9 illustrate typical response curves (the right half of the chart only is shown, to facilitate comparison). It will be noted that response begins within 1 minute and is complete in 2 1/2 minutes. Figure 9 clearly shows how much faster the response is for a large concentration change than for a small one.

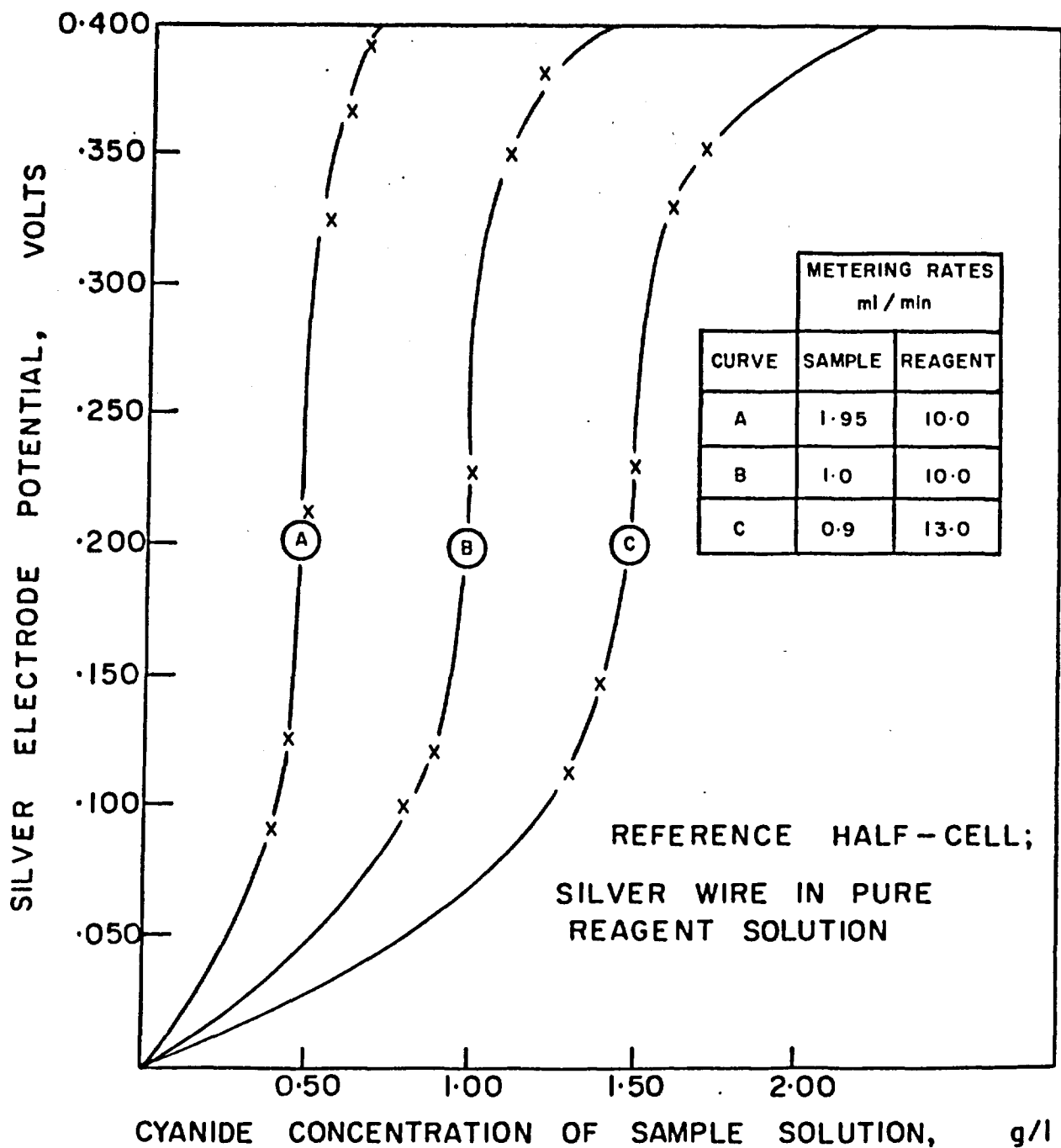


Figure 6. Experimentally determined calibration curves for the continuous titration of cyanide with ammoniacal silver:argentocyanide solution at various ratios of sample and reagent flow-rates.

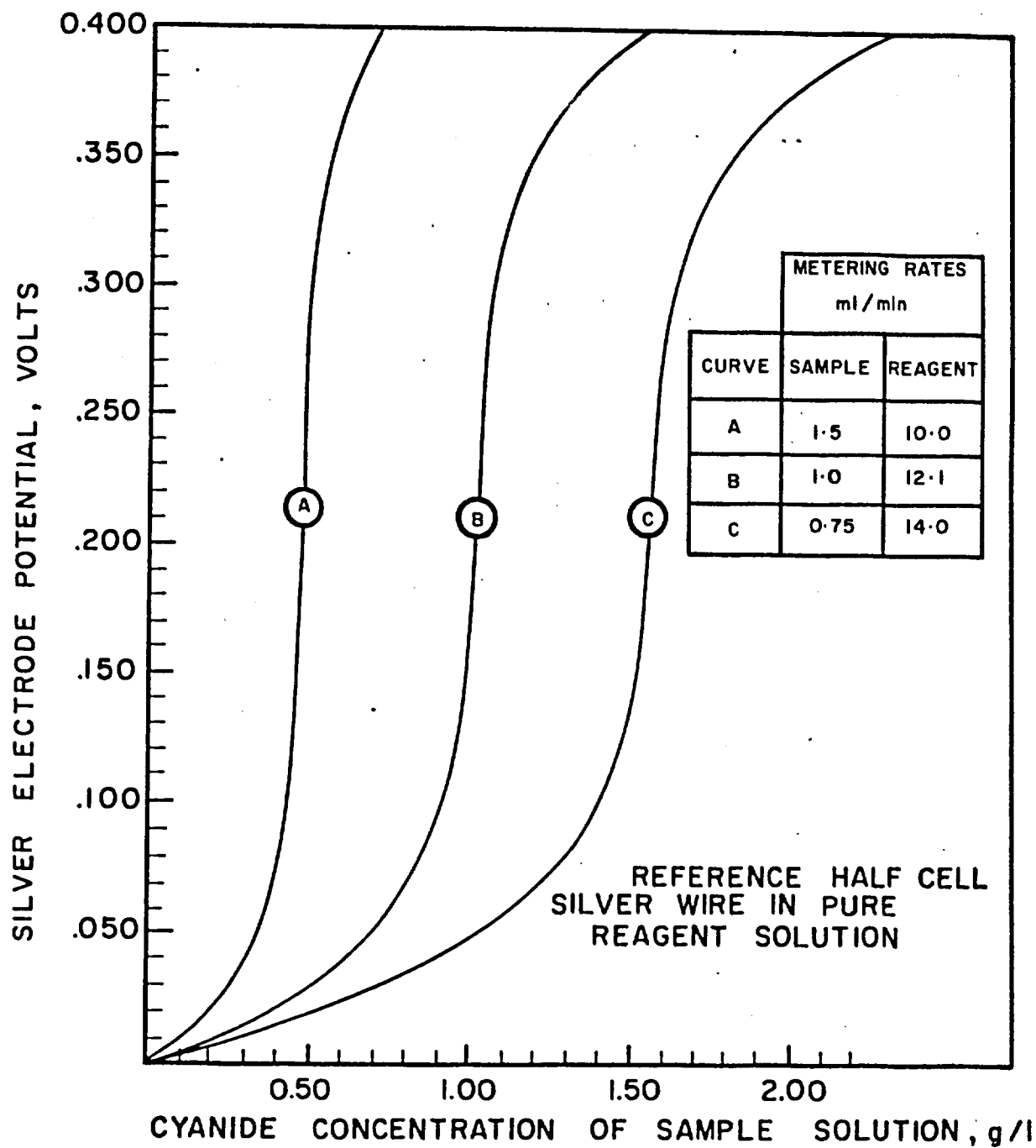
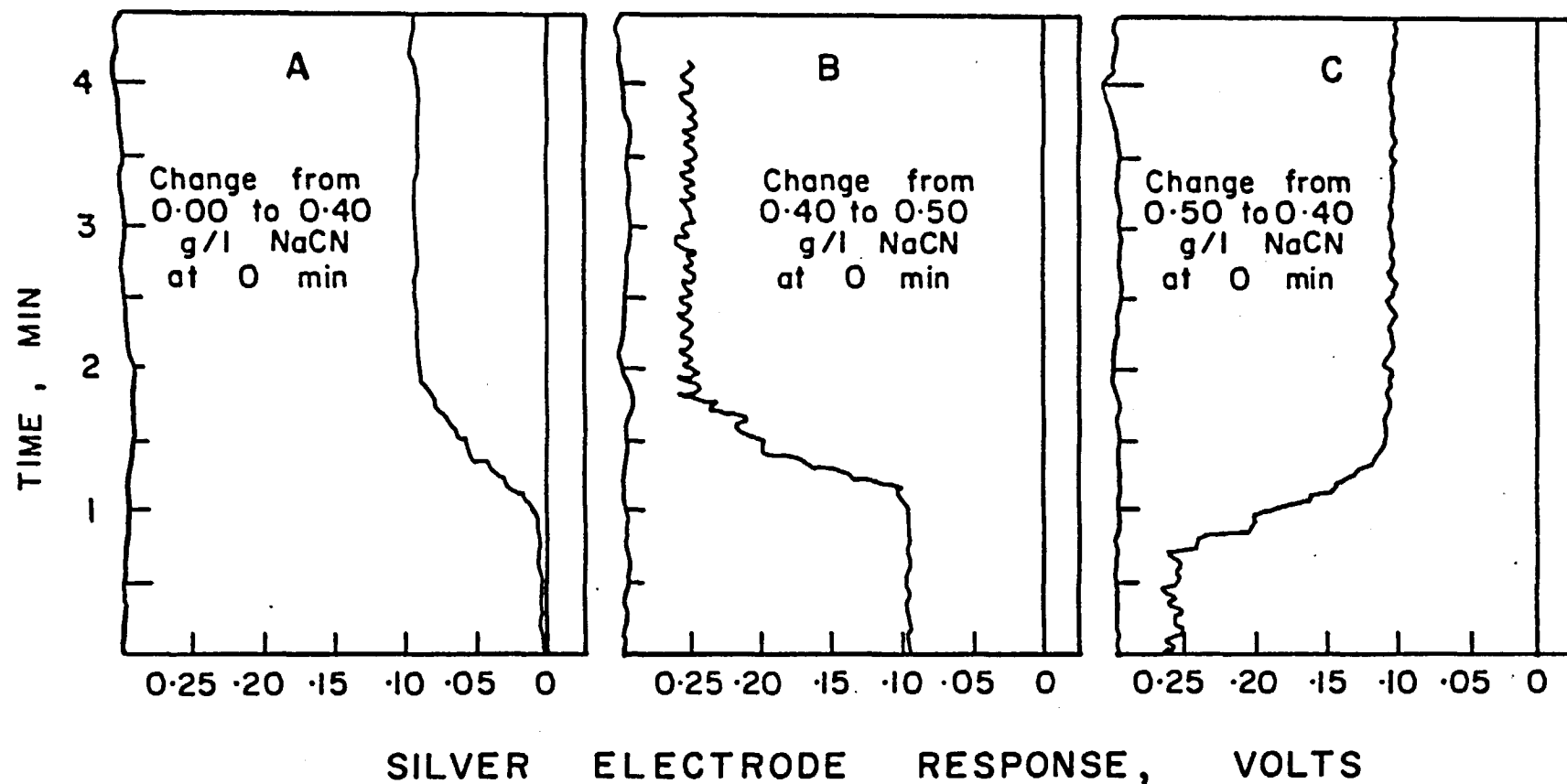
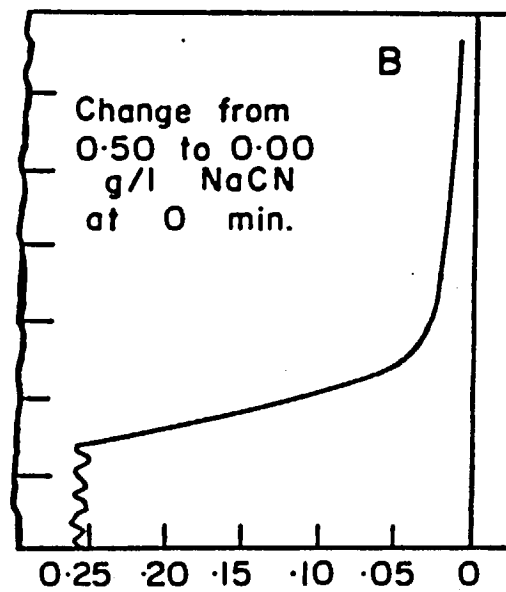
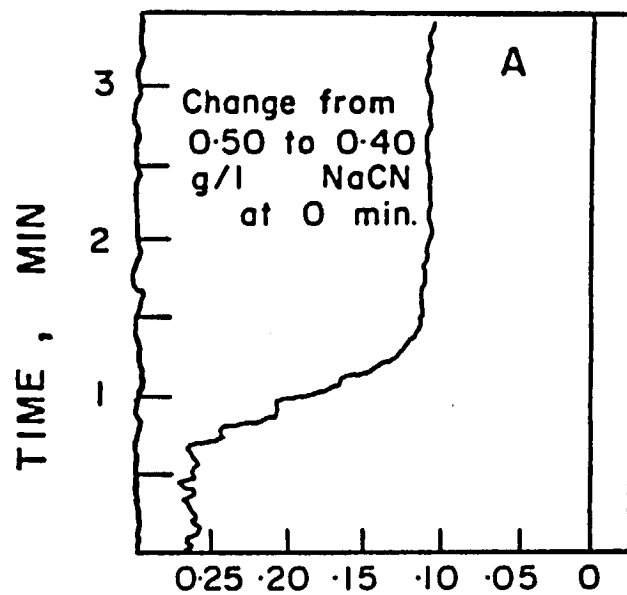


Figure 7. Calculated calibration curves for continuous cyanide titration, based on conventional direct titration.



(RIGHT HALF OF CHART ONLY)
 Figure 8. Typical rate-of-response curves (pumps set for maximum response at 0.50 g/l NaCN).



SILVER ELECTRODE RESPONSE, VOLTS

(RIGHT HALF OF CHART ONLY)

Figure 9. Effect of size of concentration change on rate of response (pumps set for maximum response at 0.50 g/l NaCN).

The short-term fluctuations can also be observed in these figures. These fluctuations correspond to the opening and closing of the check valves in the metering pumps. They are more noticeable when the cyanide concentration of the sample is near the end-point value (control value) because the electrode response is greatest there. The fluctuations could be damped out by suitable modification of the meter or recorder without otherwise affecting the operation, since their periodicity is much shorter than the overall response time.

A simple "on-off" device, employing a photocell and shutter, was attached to the recorder to illustrate the control application. A closed-loop servomechanism directly applicable to continuous titrations, and which resembles more closely the type of control that would be used in practice, has been described by Freund (9).

CONCLUSION

An apparatus for the control of free cyanide concentration by continuous potentiometric titration and which can be assembled from relatively inexpensive, commercially-available components, has been described. A modified titrant has been specifically formulated for this application, and the combination has been demonstrated to operate simply and reproducibly. The only attention required, other than routine maintenance, is the replacement of the single reagent solution when it has been used up. Details of a closed loop servomechanism to permit the system to be used for process control can be found in the literature. It is believed that the method described offers advantages in cost, simplicity of operation, and reliability, over other systems that have been proposed previously to provide continuous cyanide analysis. A particular advantage is that it measures free cyanide, the factor of actual interest, rather than total cyanide, which is the factor measured by some of the other systems.

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* In Appendix, page 19.

APPENDIX

Theoretical Basis of the End-point Detection System

The potential of a silver electrode immersed in a solution containing silver ions under equilibrium conditions is given by the Nernst equation:

$$E = E_o - \frac{RT}{nF} \ln a \quad (\text{Eq 1})$$

$$= E_o - 0.059 \log_{10} a \quad (\text{Eq 2})$$

where a is the silver ion activity.

If, as a reference cell, a silver electrode dipping into an otherwise identical solution containing a different concentration of silver ions (a_2) is used, the potential set up between these electrodes is given by:

$$E = -0.059 \log_{10} \frac{a_1}{a_2} \quad (\text{Eq 3})$$

where a_1 and a_2 are the activities of the silver ions in the two solutions, and it is assumed that junction potentials have been reduced to insignificant levels.

The dissociation of the argentocyanide ion is expressed by the equation:

$$K = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2^-]} \quad (\text{Eq 4})$$

and, hence, in a solution containing this ion the silver ion activity is given by:

$$[Ag^+] = K \frac{[Ag(CN)_2^-]}{[CN^-]^2} \quad (\text{Eq 5})$$

The argentocyanide ion activity, $[Ag(CN)_2^-]$, is given by:

$$[Ag(CN)_2^-] = Ag(CN)_2^- \text{ Total} - [Ag^+] \quad (\text{Eq 6})$$

If $\text{Ag}(\text{CN})_2^-$ Total, the total argentocyanide content of the solution, is made sufficiently high (of the order of 0.01 M, for example), then, because its dissociation is so small, the free silver ion activity is negligible in comparison and the identity

$$[\text{Ag}(\text{CN})_2^-] = \text{Ag}(\text{CN})_2^- \text{ Total} \quad (\text{Eq 7})$$

can be substituted.

Thus, if we now consider two half-cells, consisting of silver electrodes immersed in solutions containing equal concentrations of argentocyanide (at a sufficiently high value) but containing different amounts of cyanide, C_1 and C_2 , the potential between them is obtained by substituting Equations 5 and 7 in Equation 3.

$$E = -0.059 \log_{10} \frac{K(\text{Ag}(\text{CN})_2^- \text{ Total}) \times C_1^2}{C_2^2 K(\text{Ag}(\text{CN})_2^- \text{ Total})} \quad (\text{Eq 8})$$

$$= -0.059 \log_{10} \left(\frac{C_1}{C_2} \right)^2$$

$$= -0.118 (\log_{10} C_1 - \log_{10} C_2) \quad (\text{Eq 9})$$

If C_2 is the cyanide ion activity of the reference solution, which does not change, and C_1 that of the solution containing the unknown cyanide ion activity, the expression becomes

$$E = -0.118 (\log_{10} C_1 - b), \quad (\text{Eq 10})$$

where b is a constant.

In the continuous titration procedure described above, the solution presented to the silver electrode is obtained by mixing a reagent containing, in addition to the required concentration of argentocyanide ion, a known excess of silver ions at approximately the same concentration as that of the cyanide ions in the sample. Both the silver and the cyanide ion concentrations are lower than the argentocyanide concentration by a factor of ten, so that, for the solutions in which cyanide is in excess after mixing the sample and reagent, the basic considerations of the above argument are not altered. Moreover, since the magnitude of the equilibrium constant for the silver-cyanide system is so much greater than that of the silver-ammonia system, the presence of ammonia can be neglected on this side of the titration curve. In this case, therefore, since 1 mole of silver is stoichiometrically equivalent to 2 moles of cyanide, Equation 10 becomes:

$$E = -0.118 \{ \log_{10} (C-S/2) - b \} \quad (\text{Eq 11})$$

where S = the amount of silver in the mixed solution that is derived from the excess silver in the reagent, and

C = the amount of cyanide in the mixed solution that is derived from the cyanide in the sample.

The constant b is once again a function of the reference solution, which, as before, is the reagent solution and in this case contains excess silver ions.

In cases where silver is in excess after mixing sample and reagent, i.e., where the cyanide content of the sample is lower than the desired control value, the theoretical treatment is more complicated and cannot be developed using the above simple material balance approach. The interested reader may refer to the more sophisticated treatment by Ricci (10)* for a rigorous mathematical analysis of this system. Once again, however, the potential is related to the cyanide concentration through the function $C-S/2$, and a reagent composition can be chosen experimentally that will yield a calibration curve of the desired form.

JCI:(PES)im

* (10). Ricci, John E., Anal. Chem. 25, 1650 (1953).