CR. The pH had no effect. Nitric acid had no effect. At low pH, sulfuric acid depressed the signal and perchloric acid enhanced it. The sulfuric acid interference was hardly affected by La; a 0.1%-La solution, however, eliminated the perchloric acid enhancement. EDTA is insoluble and Sr precipitates out with sulfate at low pH; thus, they cannot be used as releasing agents.

CA AND MG. There is no effect upon signal intensity within the pH range of 0 to about 9. At higher pH there occurs a strong signal depression of about equal intensity for both metals. La and Sr had little effect on this interference. A 0.8%-EDTA solution completely removed the interference with magnesium, up to a pH of 12.1, but could not quite completely remove it for calcium. It appeared that EDTA may be the preferred reagent to use at high pH because it can successfully compete with the metal oxides (or hydroxides) to form complexes which can be easily decomposed in the flame. Sr and La compete for the anion of the metal, such as Cl⁻, and have little effect on magnesium and calcium when the latter are pre-

sent as the oxides. Nitric acid and sulfuric acid strongly depressed the standard Ca or Mg signal at low pH; the extent of signal depression was comparable to that observed for the anions of the acids as the sodium salts in neutral solution, indicating the interference was due to the acid anion rather than to the hydronium ion. A 0.4%-Sr solution eliminated the nitric acid interference. The sulfuric acid interference could not be eliminated by any of the releasing agents. Perchloric acid did not interfere. Bratzel and coworkers have reported on the influence of hydrochloric and nitric acids on the AFS of Cd (16).

(16) M. P. Bratzel, Jr., J. M. Mansfield, Jr., and J. D. Winefordner, *Anal. Chim. Acta*, **39**, 394 (1967).

Determination of Gold(I) in Cyanide Solutions by Solvent Extraction and Atomic Absorption Spectrometry

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A method is described for the determination of gold(I) in cyanide solutions. The gold(I) cyanide is extracted directly into an organic solvent which contains a quaternary ammonium salt. The gold content of the organic phase is determined by atomic absorption spectrometry. By varying the volume ratio of aqueous to organic phases between 1:1 and 100:1, gold concentrations between 2.5×10^{-4} to $5 \times 10^{-8} M$ (50 to 0.01 mg/liter) can be determined. Diisobutyl ketone is recommended as a suitable organic solvent because of its very low solubility in water, and because it produces a satisfactory flame. The method is faster than methods reported previously, the precision and accuracy are good, and no interference by other elements could be detected.

ATOMIC ABSORPTION SPECTROMETRY is a convenient and selective method for the determination of gold in solution. Gold concentrations as low as approximately $5 \times 10^{-6} M$ in aqueous solutions may be determined directly (1–4). Greaves (5) reported that solvent extraction of gold(III) bromide into methylisobutyl ketone led to an enhancement of the signal obtained when gold was determined by atomic absorption spectrometry. Strelow (6) used the same organic solvent to extract gold(III) chloride and was able to determine gold

values as low as $5 \times 10^{-8} M$ in cyanide waste solutions after oxidizing the gold(I) to gold(III). This oxidation step was avoided by Mallett (7) who extracted the gold(I) cyanide directly into n-butyl acetate containing trioctylamine. The pH of the aqueous phase had to be adjusted to pH 4 to ensure quantitative extraction of the gold.

The gold(I) cyanide complex is encountered most commonly in leach liquors used for the extraction of gold from ores. This process is normally performed at about pH 10 to 11, so that it would be convenient if the gold(I) cyanide could be extracted directly from the alkaline medium into an organic solvent.

Flett (8) studied briefly the solvent extraction of gold(I) cyanide by amines and quaternary ammonium salts, and reported that the extraction by trioctyl methyl ammonium chloride was complete over the pH range 1.4 to 11.5. Shivrin (9) studied the extraction of gold(I) cyanide by a series of quaternary ammonium salts and found the trioctyl methyl ammonium salt to be the most effective extractant of gold(I) cyanide, with the added advantage that it was inert to dissolved base metal cyanides. Trialkyl methyl ammonium salts seemed to be ideally suited for use in the solvent extraction step of an analytical technique for gold(I) cyanide determinations.

(1) B. M. Gatehouse and J. B. Willis, *Spectrochim. Acta*, **17**, 710 (1961).
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(4) H. F. Skewes, *Proc. Australasian Inst. Mining Met.*, **211–4**, 217 (1964–65).
(5) M. C. Greaves, *Nature*, **199**, 552 (1963).
(6) F. W. E. Strelow, E. C. Feast, P. M. Mathews, C. J. C. Bothma, and C. R. van Zyl, ANAL. CHEM., **38**, 115 (1966).

(7) R. C. Mallett, J. D. Taylor, and T. W. Steele, National Institute for Metallurgy, 1 Yale Rd., Milner Park, Johannesburg, *Res. Rept. No. 24, Project No.* C92/65 (1966).
(8) D. S. Flett and A. Faure, National Institute for Metallurgy, 1 Yale Rd., Milner Park, Johannesburg, private communication (1964).
(9) G. N. Shivrin, A. S. Basov, B. N. Laskorin, and E. M. Shirvina, *Tsvet. Metal.*, **39**, 15 (1966).
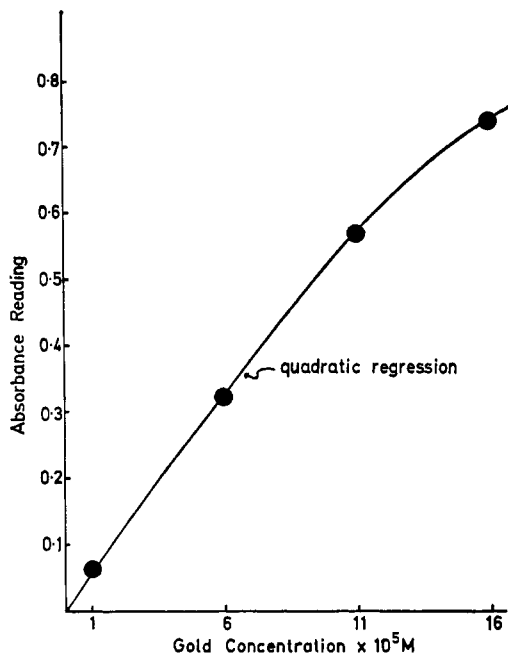
Figure 1. Analytical curve obtained from the first statistical replicate design for absorbance readings against gold(I) cyanide concentration in the original aqueous solution
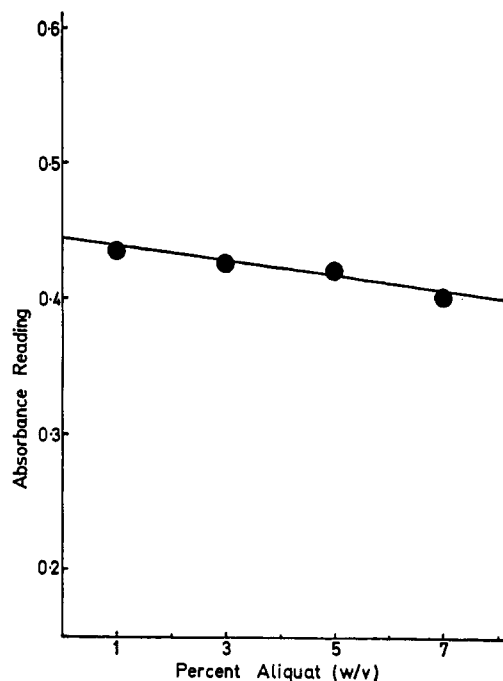

Figure 2. Relationship between absorbance readings and Aliquat 336 concentration in the organic phase as obtained from the first statistical replicate design

The organic solvent chosen was diisobutyl ketone, because it is relatively nonvolatile (bp 168° C), only very slightly soluble in water (approximately 0.05% w/v) and has favorable flame characteristics. The enhancement factor (ratio of absorbance in diisobutyl ketone to absorbance in aqueous solution) varied between 1.7 to 3.0, depending upon the concentration of salt in the aqueous phase. Although emulsification between diisobutyl ketone and the aqueous medium occurred sometimes, the presence of as little as 0.5% w/v dissolved solids in the aqueous phase usually eliminated this problem.

EXPERIMENTAL

Apparatus. A Techtron Model AA-4 atomic absorption spectrophotometer with a gold hollow cathode lamp was used for the atomic absorption measurements. The monochro-

Table I. Factors and Levels of Factors Used in the Fractional Replicate Designs to Study the Extraction of Gold(I) Cyanide into Diisobutyl Ketone Containing Aliquat 336

Design	Factor	Levels
1	Gold(I) cyanide	1, 6, 11, and 16 $\times$ 10^{-5}M
	Cyanide	10^{-7}, 10^{-5}, 10^{-3}, and 10^{-1}M
	Aliquat 336	1, 3, 5, and 7% (w/v)
	Sodium chloride	0 and 3.0M
	pH	4 and 10
2	Aliquat 336	1, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5}% (w/v)
	Gold(I) cyanide	1 and 6 $\times$ 10^{-5}M
	Cyanide	0 and 10^{-1}M
	pH	4 and 10
3	Volume ratio (aq/org)	1:1, 10:1, 50:1, 100:1
	Sodium chloride	0, 1, 2, and 3M
	Cyanide	0 and 10^{-2}M
	pH	4 and 10

mator was set at 2428Å, and the instrument settings proposed by the manufacturer were applied. The burner was supplied with coal gas and compressed air.

Reagents. Trialkyl methyl ammonium chloride was obtained from General Mills, Chemical Division, under the trade name Aliquat 336 with the alkyl groups being mainly the octyl and decyl straight chain hydrocarbons. The average molecular weight of Aliquat 336 was given as 442. Solutions of gold(I) cyanide were prepared using gold potassium cyanide manufactured by Hopkin and Williams.

Procedure. Three fractional replicate designs were used to obtain an indication of the extent to which estimates of the gold content of a solution, as given by an atomic absorption spectrophotometer, were affected by various experimental factors. The factors considered included the concentration of gold(I) cyanide, cyanide ion, and inert salts (as sodium chloride) in the aqueous phase, the pH of the aqueous phase, the concentration of Aliquat 336 in the organic phase, and the volume ratio of aqueous to nonaqueous phases.

The first design investigated primarily the effect of the concentration of gold(I) cyanide upon the absorbance reading obtained and provided information regarding the effects and interactions of the other parameters mentioned above. The second design supplemented the first one and the response to Aliquat 336 concentration was of primary importance. A volume ratio of aqueous to organic phases of 1:1 was used in the first two designs. The last design examined the effect of volume ratio of aqueous to organic phases. A constant quantity of gold (5 $\times$ 10^{-7} mole) was introduced into the aqueous phase and extracted into 10 ml of organic phase. The concentration of potassium cyanide and buffer salts was kept low so that any effect of inert salt would not be masked. Details of the factors and the levels of the factors used in the various designs are shown in Table I.

The absorbance readings plotted in the figures are the treatment means—that is, averages of absorbance readings for each level of a given factor. Only the factors found to have a significant effect are illustrated in the figures.
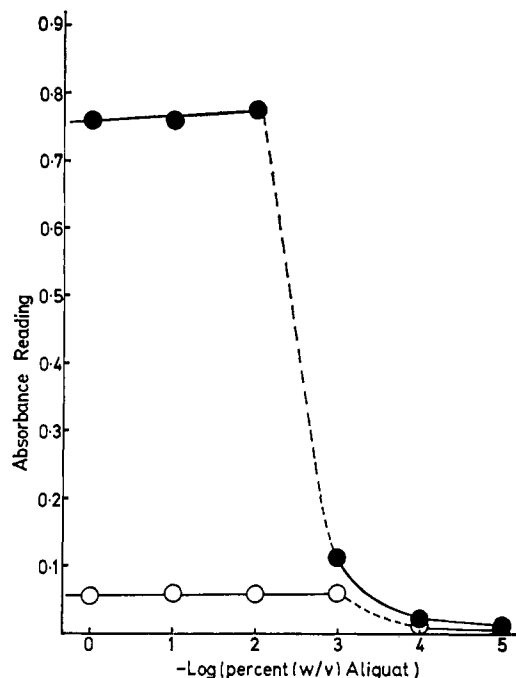
Figure 3. Relationship between absorbance readings and Aliquat 336 concentration at different gold(I) cyanide concentration levels as given by the second statistical replicate design

$\bigcirc$ for gold(I) cyanide $= 1 \times 10^{-5}M$
$\bullet$ for gold(I) cyanide $= 16 \times 10^{-5}M$

Figure 4. Effect of a change of volume ratio (aqueous to organic) upon the absorbance readings at different salt concentration levels as given by the third statistical replicate design

$\bigcirc$—NIL NaCl $\quad\quad$ $\triangle$—$2M$ NaCl
$\bullet$—$1M$ NaCl $\quad\quad$ $\blacktriangle$—$3M$ NaCl

RESULTS

The analysis of the results obtained from the first design indicated that a linear regression of absorbance on gold concentration accounted for 97% of the variation in the absorbance readings. A somewhat better fit (98%) was obtained when a quadratic regression line was fitted. This results in the slightly curved calibration line usually obtained by atomic absorption spectrometric techniques (Figure 1). The only other significant effect was a linear decrease in absorbance reading with increasing concentration of Aliquat 336 between 1 to 7% w/v (Figure 2). The absolute viscosity of the organic phase increased with increase of Aliquat 336 concentration. This could have affected the rate of feed of the sample to the burner.

By means of the second design, it was confirmed that 100% extraction of the gold(I) cyanide could be ensured as long as the organic phase contained an adequate amount of Aliquat 336. A molecular ratio of Aliquat 336 to gold(I) cyanide of about unity was the minimum required (Figure 3). Cyanide concentration and the pH value of the aqueous phase had no effect upon the absorbance readings obtained.

The analysis of results obtained with the third design indicated that the solubility of diisobutyl ketone in water could affect the results and that an increase in the volume ratio caused an increase in the absorbance readings (Figure 4). This behavior was more marked when the ionic strength of the aqueous phase was kept low. In the absence of any additional inert salt, an increase of about 9% in the absorbance reading was observed for an increase of volume ratio from 1:1 to 100:1, whereas when $3M$ sodium chloride was added, virtually no change in the absorbance reading occurred for a similar change of volume ratio. This may be explained by the decrease in the solubility of diisobutyl ketone in water under these conditions.
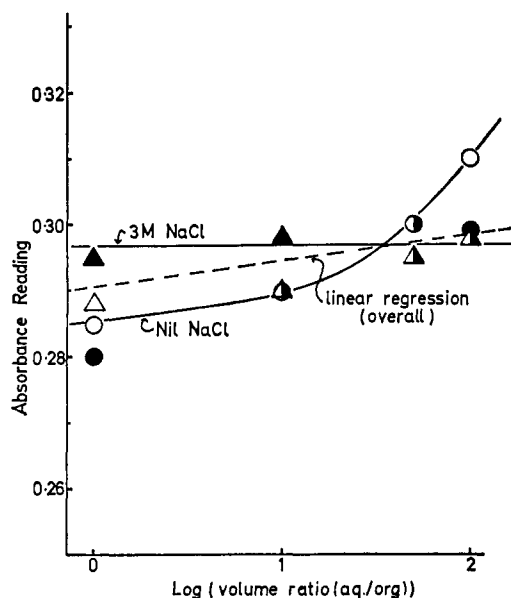
DISCUSSION

These results provided a guide to a rapid means for the determination of gold(I) cyanide in solutions over a relatively wide concentration range. The lower limit of this range may be extended by using volume ratios of aqueous to organic phases of up to 400:1. For volume ratios of this magnitude, the relatively large solvent losses would have to be taken into account by obtaining a calibration curve under conditions similar to those obtained in the test solutions.

The gold(I) cyanide is extracted directly into the organic phase which contains Aliquat 336. There is no need for control of the pH between values of 4 to 10, nor for the presence of controlled quantities of cyanide ion in the aqueous phase. Additional experiments confirmed that this procedure may be used with confidence at pH values of up to 11.5. If sufficient Aliquat 336 was present in the organic phase, no difficulties were encountered due to the presence of foreign ions.

Thus gold values between $6 \times 10^{-5}M$ to $6 \times 10^{-7}M$ were determined at pH 4 and 10 in $10^{-2}M$ cyanide solutions to which as much as $10^{-3}M$ of Zn(II), Mn(II), Ni(II), Co(II), Ag(I), Al(III), Mg(II), Ca(II), Cu(II), $Fe(CN)_6{}^{3-}$, $Fe(CN)_6{}^{4-}$, $SO_3{}^{2-}$, $H_2PO_4{}^{2-}$, or $NH_4{}^+$ had been added. None of these ions interfered with the determination of the gold, though many of them were extracted into the organic phase.

Table II. Determination of Gold in Leach Liquors

Sample no.	Fire assay	Atomic absorption
1	$7.84 \times 10^{-8}M$	$7.75 \times 10^{-8}M$
2	$5.72 \times 10^{-7}M$	$5.90 \times 10^{-7}M$
3	$1.046 \times 10^{-5}M$	$1.01 \times 10^{-5}M$
4	$2.88 \times 10^{-5}M$	$2.84 \times 10^{-5}M$
5	$4.29 \times 10^{-5}M$	$4.24 \times 10^{-5}M$

The precision of the method was established by analyzing solutions containing (a) $1 \times 10^{-8}M$, (b) $1 \times 10^{-7}M$, and (c) $5 \times 10^{-5}M$ gold(I) cyanide. From seven 1-liter aliquots the standard deviations obtained were (a) 0.07×10^{-8} and (b) $0.01 \times 10^{-7}M$ and from five 20-ml aliquots the standard deviation for (c) was $0.05 \times 10^{-5}M$. The accuracy of this method was gauged by comparison with the fire assay technique (Table II).

A duplicate determination may be performed within 10 minutes. The method is, in fact, so simple and rapid that it has been used as the basis for an automatic "on line" analyzer of gold-bearing cyanide waste solutions (10).

RECOMMENDED PROCEDURE

The most favorable spectrophotometric response, giving absorbance readings between 0.2 and 0.7 unit, may be obtained by selecting a suitable volume ratio of aqueous to organic phases for the solvent extraction of the gold. When diisobutyl ketone is used for this purpose, this ratio should be such that the concentration of gold in the organic phase lies within the range of 4 to $14 \times 10^{-5}M$. However, adequate results may be obtained if this concentration range is expanded to 1 to $18 \times 10^{-5}M$.

For most purposes a 1% solution of Aliquat 336 in diisobutyl ketone will be adequate for the extraction of the gold from the aqueous phase. A quantity sufficient for the determination of the gold may be collected if as little as 5 ml of the diisobutyl ketone solution is used for the solvent extraction.

The required volumes of the aqueous gold-bearing solution and the diisobutyl ketone solution are agitated in a separating funnel for about 1 minute; when small volume ratios are used, complete extraction of the gold occurs within 15 seconds. After the phases have separated, the ketone layer is collected and aspirated into the flame of the atomic absorption spectrophotometer.

Because absorbance readings are affected by slight changes in the flame, and by instrument settings, a series of standard solutions containing gold concentrations of the same order as those in the test solutions should always be used to construct a calibration curve. These standard gold solutions, made up to about $0.1M$ NaCl, may conveniently be prepared by dilution of a stock standard gold solution containing about $10^{-2}M$ gold(I) cyanide. The solutions of gold in diisobutyl ketone, as prepared by this solvent extraction of the standard aqueous solutions, are stable, and may be retained without deterioration for calibration of the atomic absorption spectrophotometer at any time.

(10) R. J. Calteaux, D. E. Naude, and A. J. Rossouw, Corner House Laboratories, P. O. Box 1056, Johannesburg, private communication (1967).

Direct Mass Spectrometric Determination of Atmospheric Carbon Dioxide

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The direct mass spectrometric determination of atmospheric carbon dioxide cannot be performed with any useful degree of accuracy because of the high concentration of oxygen in the atmosphere. By removing the oxygen with phosphorus, it is possible to admit sufficiently high pressures of the remaining gas to determine the carbon dioxide with an inaccuracy of less than 1%. Because the argon content of the atmosphere is presumed constant, a direct comparison of the carbon dioxide to argon ratio should provide a fixed reference for future surveys. The method is rapid and requires little equipment other than a mass spectrometer. Results obtained on analysis of rural air in the vicinity of Washington, D. C., are presented.

THE DIRECT MASS SPECTROMETRIC DETERMINATION of atmospheric carbon dioxide cannot be performed with an error of much less than 30% using conventional techniques. The reasons for this lie in the fact that inlet pressures sufficiently high to allow an accurate measurement of the ion current caused by carbon dioxide result in such high pressures of oxygen that filament failure can occur. Also, carbon dioxide is generated in the ionization region possibly through reaction between oxygen and the coating of tungsten carbide on tungsten filaments resulting in erroneously high results.

It is possible to determine carbon dioxide in nitrogen by direct mass spectrometry employing inlet pressures considerably higher than those normally employed (1). If oxygen is first removed from atmospheric air, it should be possible to employ a similar technique for the direct determination of atmospheric carbon dioxide without the need for concentration techniques or other techniques which might alter the carbon dioxide concentration.

The method described here utilizes phosphorus to remove

(1) E. E. Hughes and W. D. Dorko, ANAL. CHEM., **40**, 750 (1968).