The automatic determination of trace amounts of gold in gold-plant barren solutions

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SYNOPSIS

A maximum of ten process streams (Merrill barren solutions) can be monitored sequentially with this on-line analyser, and gold concentrations as low as 0,005 mg/l can be determined. The design is a further development of the Tell-tale analyser constructed by the Corner House Laboratories during the period 1965–69.

The barren solution is preconcentrated automatically by solvent extraction, the solvent being a solution of 1 per cent Aliquat 336 in di-isobutyl ketone. An aqueous-to-solvent ratio of 40:1 is maintained. The extracted gold in the organic phase is determined by flame atomic absorption, each analysis taking approximately 11 minutes.

The long-term reproducibility of the absorbance readings over a 24-hour period of repetitive sampling of four simulated process streams varied from 6,9 to 4,1 per cent relative standard deviation for gold concentrations of 0,01 to 0,05 mg/l.

SAMEVATTING

'n Maksimum van tien aanlegstrome (Merrill uitskot oplossings) kan opeenvolgend met hierdie gekoppelde analiseerder gemonitor word en goud konsentrasies so laag as 0,005 mg/l kan bepaal word. Die ontwerp is 'n verdere ontwikkeling van die 'Tell-tale' analiseerder wat deur die Corner House Laboratoriums gedurende 1965–69 saamgestel is.

Voorafkonsentrasie van die uitskot oplossings vind outomaties plaas deur middel van vloeistofekstraksie. Die oplosmiddel wat gebruik word is 'n oplossing van 1 persent Aliquat 336 in diïsobutielketoon. 'nWater tot oplosmiddel verhouding van 40:1 word gehandhaaf. Die geëkstraheerde goud in die organiese fase word deur middel van vlam atoomabsorpsie bepaal. Die tydsduur van elke analise is ongeveer 11 minute.

Die langtermyn reproduseerbaarheid van absorbansie waardes tydens 'n 24 uur herhalende monsterneming van vier nagebootste aanlegstrome het gewissel van 6,9 tot 4,1 persent relatiewe standaardafwyking vir goudkonsentrasies tussen 0,01 en 0,05 mg/l.

Introduction

During 1965–69, an automatic gold analyser was developed by Corner House Laboratories to monitor the gold content of Merrill barren solutions. Modified working models of this Tell-tale analyser are still in operation at the E.R.P.M. and Blyvooruitzicht Gold mines, and disused models have been located at two Anglo American gold mines on the Free State gold fields.

The operation of the Tell-tale analyser is based on the continuous solvent extraction of gold from aqueous solution into a dilute (approximately 1 per cent) solution of a commercial tertiary long-chain amine, Aliquat 336 in butyl acetate in the approximate aqueous-to-organic ratio of 40:1, followed by flame atomic-absorption analysis of the organic extract for gold. An improved solvent-extraction system has been described by Groenewald[1] for the manual extraction and analysis of very low concentrations of gold in cyanide solutions, but no description of continuous solvent extraction and atomic-absorption analysis of gold using Aliquat 336 and di-isobuty ketone could be found in the literature.

When the Anglo American Corporation decided that automatic monitoring of gold values in barren solutions should be the ultimate aim for all their gold plants, the Anglo American Research Laboratories (AARL) investigated the possibility of improving and modernizing the original Tell-tale analyser.

Discussions were held with staff from AAC gold plants and other interested parties to decide on the requirements for a complete automatic system that would suit the conditions at virtually every South African gold plant. It was decided that the analyser should be capable of the following:

1. sampling and analysing up to ten process streams in sequence in a minimum of time,
2. achieving a sensitivity of at least 0,01 mg of gold per litre,
3. producing accurate and reproducible results over long periods of continuous operation with a minimum of maintenance and calibration,
4. activating an audio-visual alarm in the control room of the gold plant if the gold concentration exceeds a pre-set value,
5. providing a continuous record of gold values in samples of all the barren streams,
6. allowing for remote switching of the streams to be sampled, and
7. incorporating an automatic shut-down device that will operate in the event of any supply failure to the analyser, e.g. power, water, air, and acetylene supplies for the atomic-absorption spectrometer, including a separate alarm to notify plant staff of the shut-down.

Design of the Tell-tale Analyser

Since a description of the original Tell-tale analyser could be found only in internal reports of the Corner House Laboratories[2, 3], and since the design of the automatic gold analyser developed at AARL incorporated a number of features of the Tell-tale analyser, it is appropriate to describe it here briefly.

The continuous solvent-extraction unit consists of a multi-tube peristaltic pump that delivers sample

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solution (barren gold solution) and organic extractant at fixed rates of 19,5 ml/min and 0,42 ml/min respectively to a mixing coil filled with glass beads.

The phases are separated in a U-tube settler, the aqueous overflow from one limb of the tube being run to waste and the organic extract overflowing from the other limb being collected for analysis by flame atomic-absorption spectrometry. Since the rate of sample consumption by an atomic-absorption spectrometer is about 5 ml/min, it is not possible to spray the organic gold extract into the nebulizer continuously, and it is accumulated for 5 minutes. During this time, the burner is cleaned by the aspiration of dilute aqua regia and then water into the flame, followed by the aspiration of a calibration standard consisting of an aqueous solution of gold cyanide with a gold concentration of approximately 1 mg/l. The actual analysis is performed once every five minutes. The analytical cycle thus consists of the feeding into the spectrometer of the following solutions in sequence:

(a) water (90 seconds),
(b) aqueous gold standard (35 seconds),
(c) water (60 seconds),
(d) dilute aqua regia (35 seconds),
(e) water (50 seconds), and
(f) barren-solution extract (30 seconds).

The four liquids are aspirated into the flame from four small vessels close to the spectrometer. A pneumatic system lifts and transports the intake tube to the nebulizer from one vessel to the next. The sequence of operation is controlled by studs on a drum attached to a synchronous clock motor at appropriate intervals, which triggers the various sample intakes of the analytical sequence via turbulence amplifiers. A stepping relay allows each analytical cycle to be repeated twice before the analysis of another barren-solution stream. Three cycles are required to minimize cross-contamination of one stream by the stream analysed immediately before. Up to eight streams can be analysed.

The Tell-tale analysers used by E.R.P.M. and Blyvooruitzicht Gold Mines have been modified to some extent in the light of the experience gained during long periods of operation. Among other modifications, the 35-second flush with aqua regia was discarded because of extensive corrosion of the burner head. During that time water is now aspirated into the flame. A multi-head micro-metering pump of the positive displacement type has taken over the function of the multi-tube peristaltic pump, since maintenance requirements on the former are less severe. The original glass-spiral mixer has been replaced by a stainless-steel Kennix type of static mixer.

Both instruments, which use the discontinued Techtron AR-200 atomic-absorption spectrometer equipped with a gold resonance detector, have been working for several years and perform satisfactorily provided a regular maintenance schedule is adhered to[4]. The original gold resonance detector was replaced in 1970 by monochromator unit set for the gold line. The Tell-tale analysers merely provide an indication of how the precipitation circuit of the gold plants is performing: quantitative analyses for gold in the barren solutions, which are not possible without careful calibration of the instruments, are not considered necessary for control purposes[4].

Design and Performance of AARL Automatic Gold Analyser

In view of the experience gained by E.R.P.M. and Blyvooruitzicht Gold Mines with the Tell-tale analyser, it was decided to base the design of the automatic gold analyser on the following principles.

(1) The solvent-extraction (mixer–settler) unit would be similar to that of the Tell-tale analyser, except that the total volume of the system, particularly the U-tube settler, would be as small as possible in order to minimize 'memory effects' (which might be carried over from the analysis of one stream to the next). This would automatically shorten the analytical times.
(2) The method used for the collection of the organic extract and for the feed to the atomic-absorption spectrometer would be simplified.
(3) Quantitative results would be produced by a single analysis so that there would be no confusion of data as with presentation by a strip-chart recorder. The strip-chart record would facilitate identification of the stream sampled and its analysis.
(4) The timing of the analytical sequence and stream switching would be controlled electronically, instead of by a combination of electro-mechanical and pneumatic controls.
(5) The mechanical and electronic components of the system would be easy to service and replace.

A schematic diagram of the mixer–settler unit used in the AARL automatic gold analyser is shown in Fig. 1.

Two-head positive-displacement micro-metering pumps are used to deliver barren solution (50 ml/min) and 1 per cent Aliquat 336 in di-isobutyl ketone (1,25 ml/min) continuously via a manifold and a glass mixing spiral of 4 mm internal diameter filled with 2 mm glass beads into a 60 cm^3 U-tube settler. The phase separator is provided with a drainage point, which allows it to be emptied, after the analysis of a barren solution, by operation of a solenoid valve (B) connected to a water pump. The aqueous overflow from the settler is continually drained to waste via a water pump, and the organic overflow is allowed to drip into a tilting glass collector (C) fixed to a 'post office' type of relay. When the relay is activated, sufficient sample is collected for subsequent discharge into a glass sample funnel, which is connected to the nebulizer tube of a Varian Techtron AA-175 atomic-absorption spectrometer by a Luer lock attached to the bottom inlet of the funnel and a 22-gauge syringe needle.

During flushing and equilibration of the solvent-extraction system when switching from one barren stream to the next, tap water is passed into the sample funnel via a tangential inlet tube connected to a solenoid valve (D), and relay C is de-activated. A tangential outlet about 5 mm below the inlet is connected to a water pump, allowing a constant flow of water through the funnel when actual analysis is not taking place. During this time, the organic extract is allowed to run to waste onto the swirling water surface in the sample funnel.

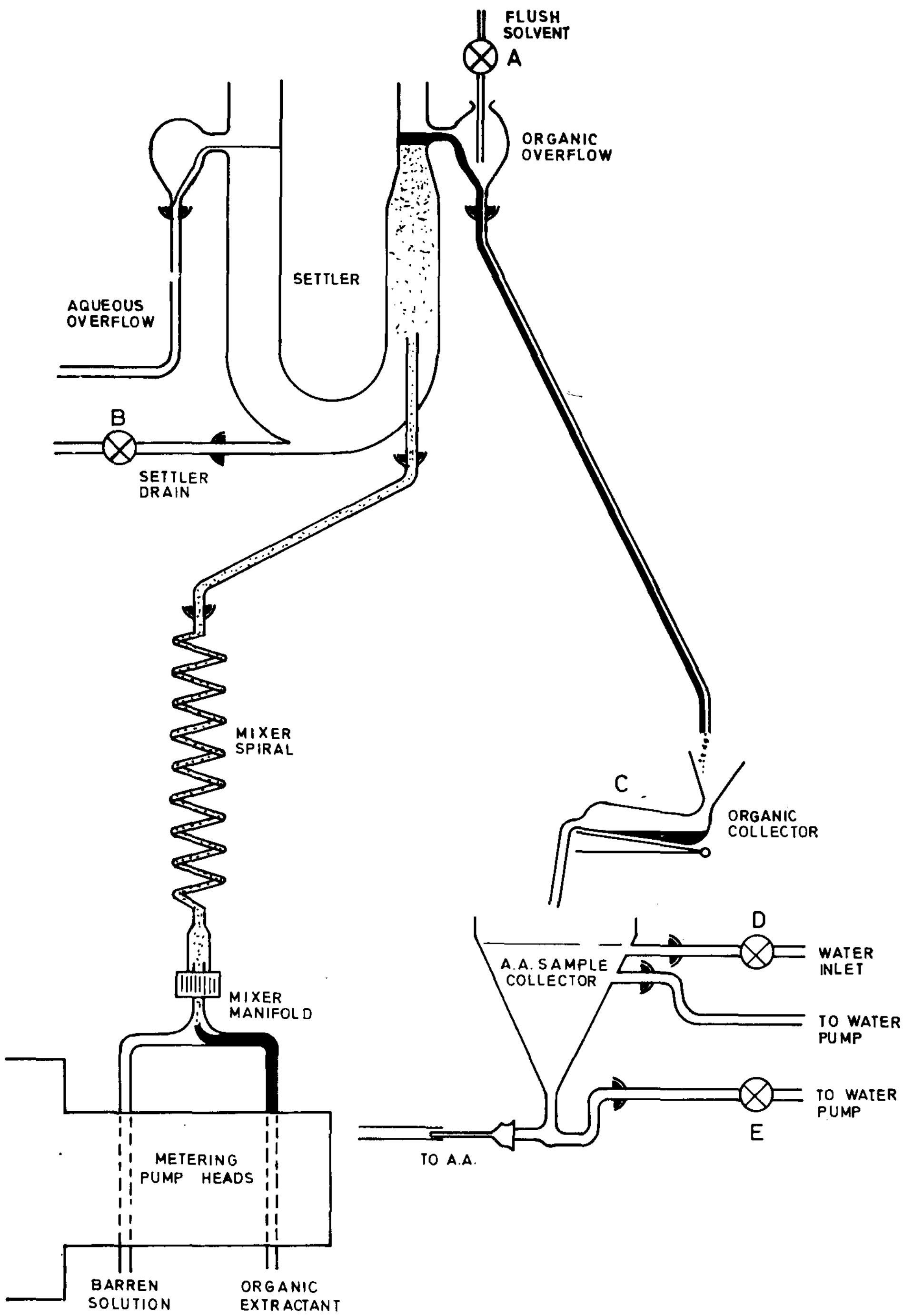

Fig. 1—Design of mixer–settler for the automatic determination of gold

Before the collected organic extract is discharged for measurement of the absorption, water is evacuated from the funnel via solenoid valve E connected to a water pump.

After most of the organic extract has been consumed by the nebulizer/burner during measurement of the gold absorbance, the remainder is evacuated from the sample funnel. A stream of methyl isobutyl ketone is allowed to flow by gravity through a capillary tube issuing near the organic overflow of the U-tube settler in order to flush through any residual gold containing organic extract. This flushing was found to be necessary since significant quantities of gold–Aliquat 336 complex coated the glass surfaces of the sample funnel. The subsequent introduction of loaded solvent during the next analytical cycle redissolved the adsorbed gold complex, resulting in erroneous absorbance values, particularly if the concentration ratio of the gold in the two streams sampled was larger than about 10:1. All the equipment in contact with loaded solvent is made of glass throughout, since it was found that any plastic material, such as PVC, polyethylene, or nylon, resulted in significantly longer equilibration times, possibly owing to some adsorption of the gold–Aliquat 336 complex on these

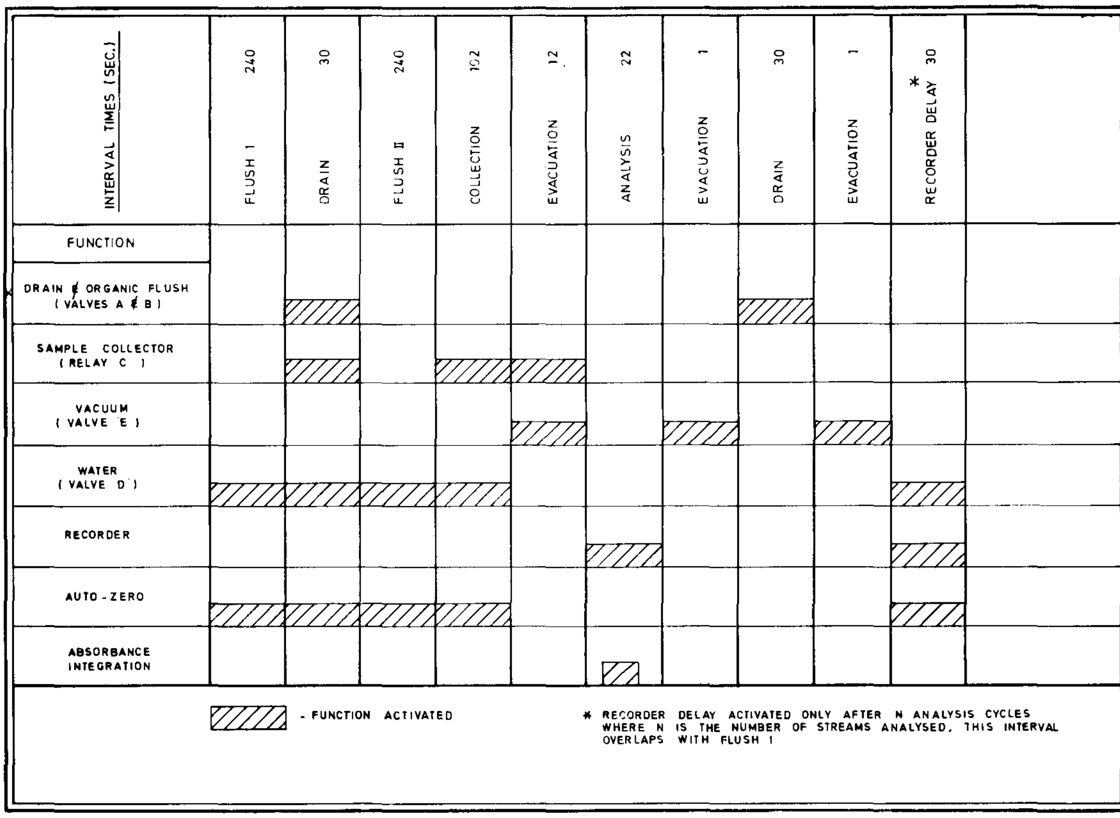

Fig. 2—Timing sequence in the automatic determination of gold

materials. For ease of servicing and replacement, all the connections have ball-and-socket joints.

The complete analytical cycle consists of the steps shown in Fig. 2, and is controlled by a gold-analysis control unit, which is basically a multifunction timer with a series of relay outputs designed and constructed by the Anglo American Electronics Laboratories. The relays control the operation of the solenoid valves of the solvent-extraction unit and of the inlets for the sample streams. In addition, relay outputs are used to perform the following functions:

(a) to zero the atomic-absorption spectrometer whenever the sample funnel is filled with tap water;
(b) to initiate integration of the absorbance signal from the spectrometer approximately 10 seconds after the organic extract is introduced into the sample funnel;
(c) to control the feed mechanism of the recorder chart, which is activated only during the actual analysis step of the cycle to conserve chart paper; an additional 30-second chart feed is provided after a set number of streams have been analysed and before the next series of analyses is conducted, therefore facilitating identification of the stream analysed;
(d) to activate an audible or visual alarm if a set maximum absorbance value is exceeded.

The four most important intervals of the analytical cycle (first and second flush, sample collection, and analysis) can be set externally on the gold-analysis control unit via thumbwheel switches, and the remaining intervals are adjusted by internal 1-to-128-second digital switches. A repeat-analysis switch allows rapid analyses to be conducted on the same stream every 2,3 minutes, since the 9-minute sample equilibration interval is short-circuited at that setting.

A set of ten switches and associated light-emitting diodes allows any one of ten streams to be either analysed or by-passed. There is provision for remote selection of sample streams to permit the automatic gold analyser to be integrated with the operational control of the Stellar or Merrill filters of a gold plant if desired. All the electronic components are mounted on plug-in printed circuit boards, which permits rapid servicing.

A utilities control unit was constructed that, by means of pressure switches and relays, causes the automatic analyser to stop if the pressure of the gas supplies for the laminar-flow burner (i.e., air and acetylene) or the pressure of the tap-water supply falls below set values. The gold analyser can be re-started manually only after the faulty condition has been rectified. In addition, the flame temperature is monitored continually by means of a thermocouple, and accidental extinction of the flame results in automatic shut-down. The unit is provided with an output for a remote audio-visual alarm to alert plant staff of a service failure. The complete AARL automatic gold analyser is shown in Fig. 3.

Performance of the Automatic Gold Analyser

The complete analyser was tested several times in the laboratory over long periods of continuous operation. An example of the chart record for a 24-hour run on

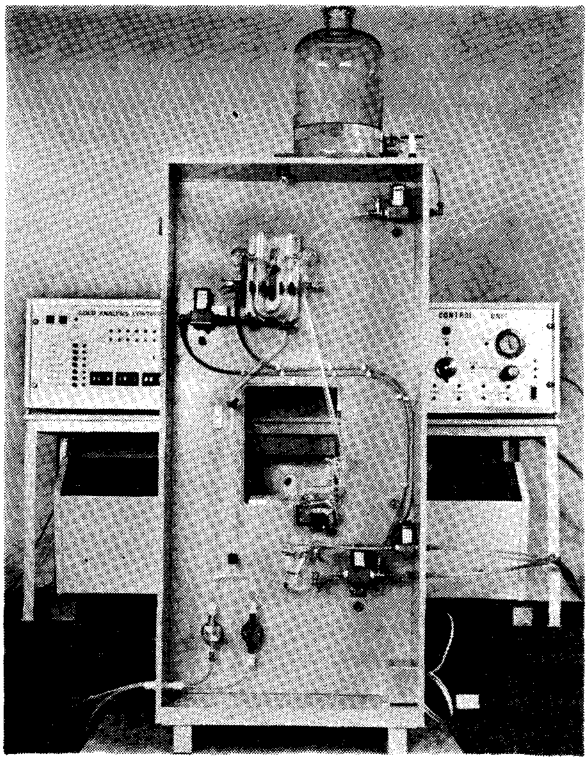

Fig. 3—The AARL automatic gold analyser

four plant solutions is shown in Fig. 4. Stream 1 consisted of Ergo barren solution (0,002 mg of gold per litre), and the other three streams were made up from the same barren solution and potassium auricyanide to yield gold concentrations of 0,010 mg/l, 0,023 mg/l, and 0,050 mg/l.

TABLE I

STATISTICAL ANALYSIS OF THE RESULTS OF A 24-HOUR RUN
Number of analytical cycles: 33

Stream no.	Gold concn mg/l	Mean absorbance	One standard deviation	Relative standard deviation, %
1	0,002	—	—	—
2	0,010	0,027 18	0,001 88	6,9
3	0,023	0,066 12	0,003 28	5,0
4	0,050	0,144 85	0,005 96	4,1

It can be seen from the recorder trace that the gold values in the Ergo solution (0,002 mg/l) are not measurable. The mean of 33 absorbance values for each of the other three streams and their standard deviations are summarized in Table I, and the calibration curve is shown in Fig. 5, together with the standard deviation of the absorbance for each stream. It is estimated that the detection limit of the system is 0,005 mg. Each analysis was completed in 11,3 minutes, of which a total of 9 minutes is required for the flushing and equilibration of the mixer-settler unit. This long equilibration time ensures that a barren solution with the unlikely gold concentration of 0,2 mg/l will not affect the subsequent analysis of a stream of 0,002 mg/l. If this strict requirement is relaxed, equilibration times can be halved and an analysis performed every 6,8 minutes.

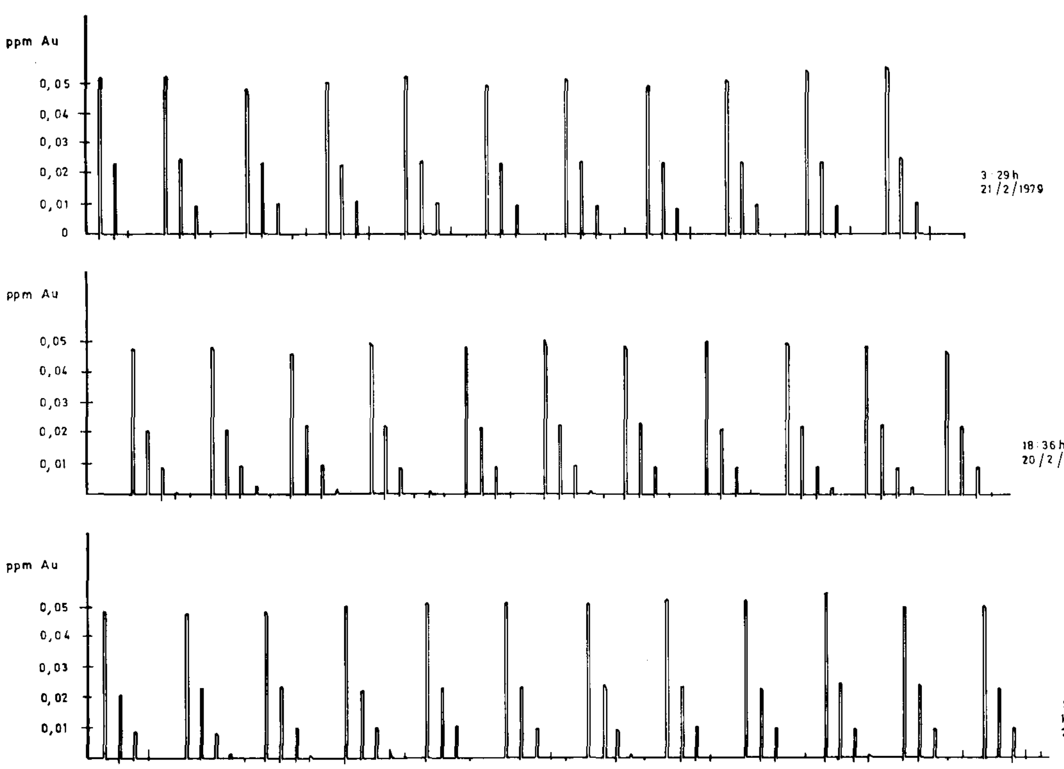

Fig. 4—Results of a 24-hour continuous test on four sample streams of different concentrations

It is evident from the recorder trace that the automatic zeroing of the spectrometer on tap water instead of fresh solvent produces satisfactory long-term stability with good analytical precision, although it results in a slight shift in the calibration graph (Fig. 5), which no longer passes through the origin.

In practice, the response of the spectrometer is calibrated against a synthetic aqueous standard with a gold concentration of, say, 0,05 mg/l, which is passed through the solvent-extraction unit in the same way as a plant barren solution. In view of the long-term

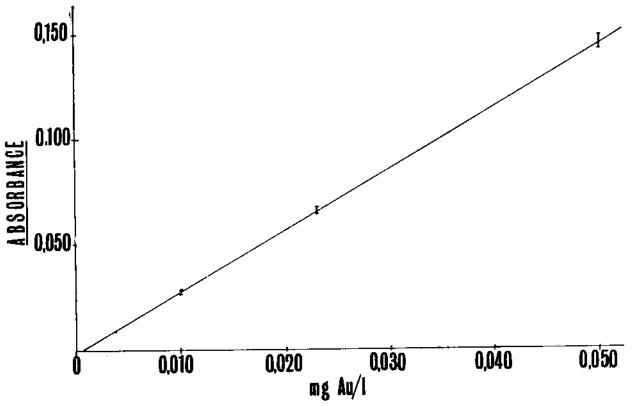

Fig. 5—Calibration graph for the AARL automatic gold analyser

stability and linear response, this calibration needs to be conducted only once every 24 hours on one standard.

Gold-plant solutions have a calcium oxide concentration of approximately 0,02 per cent, and deposits of lime therefore tend to build up on the glassware of the solvent-extraction unit. If this build-up is allowed to continue, the bead-packed mixing spiral may become blocked. To overcome this, the analyser should be allowed to sample a 1 per cent solution of the sodium salt of EDTA for 10 minutes each day. The laminar-flow burner and nebulizer assembly must be serviced regularly to ensure that the system is working efficiently. As a result of the alternate aspiration of organic solvent containing Aliquat 336 and tap water, gummy deposits build up, causing partial blocking of the burner slot.

A prototype of the AARL automatic gold analyser has been installed at the Ergo gold plant, where it has been monitoring the barren effluent from three Stellar filters, as well as a barren composite solution, since November 1978. A second unit will operate at the Elandsrand gold plant in the near future.

Apart from determining the gold in barren solutions at the Ergo plant, the automatic analyser monitors effluent from a Stellar filter during precoating operations. During this time, the unit provides semi-continuous information (every 2,3 minutes) of gold in solution while a slurry of gold–zinc slimes and precoating material is recirculated. When the gold concentration has dropped to an acceptably low level, the barren solution is discharged to waste. An example of the monitoring of a precoating operation by the analyser is given in Fig. 6.

The Anglo American Electronics Laboratories are making further modifications to the gold-analysis control unit. Future models will be based on microprocessor control, which provides for a considerable expansion of capabilities as follows.

(a) The data presentation will be changed from recorder traces to print-outs giving the analytical values, the stream number, and the time of analysis.
(b) The analytical times will be shorter, since the solvent-extraction equilibration time will be made a function of the gold concentration found in the previous stream.
(c) The instrument will automatically calibrate the spectrometer response once every 24 hours on a standard gold solution, and will use the calibration factor for the succeeding 24-hour period to calculate the analytical values. Should the calibration factor (i.e., absorbance per unit of gold) vary by more than a certain fraction (e.g., 10 per cent) from a previously obtained value, the plant staff will be alerted to check the operating condition of the spectrometer and the solvent-extraction unit.
(d) The solvent-extraction unit will be flushed automatically with a solution of EDTA from a reservoir once every 24 hours.
(e) The Merrill- or Stellar-filter precoating operations will be monitored automatically. If required, the analyser will be integrated with the operational control of the filter so that the gold-analysis control unit will put the filter on-line when the gold values in the barren solution have become sufficiently low during recirculation.

Conclusions

During the laboratory trials, the AARL automatic gold analyser exceeded the performance criteria listed in the Introduction. Its success in practical applications will depend to a large extent on the degree of acceptance of the unit by the operating staff of the plant concerned. It is important that gold-plant operating staff should regard the instrument as an aid to efficient operation of the precipitation circuit, and not as a policeman. It is

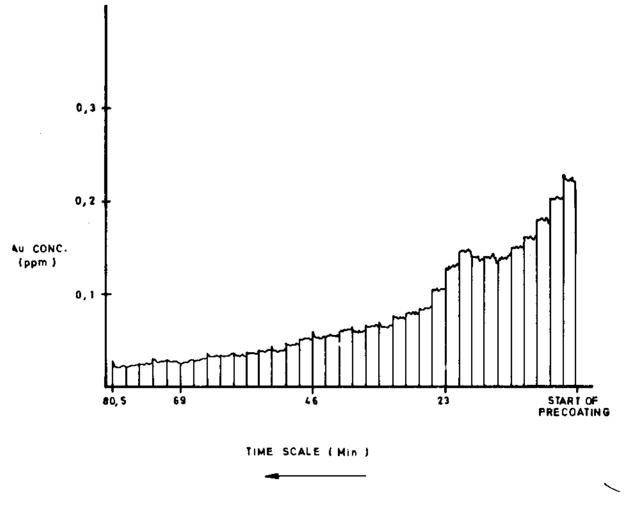

Fig. 6—Determination of gold in solution during the precoating of a Stellar filter at the Ergo gold plant (repeat analysis in concentration mode, no signal integration, time: 2,3 minutes per analysis)

felt that, once this acceptance has been achieved, they will spare no effort in maintaining the instrument in good operating condition.

Acknowledgements

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References

1. GROENEWALD, T. *Analyt. Chem.*, vol. 40. 1968. p. 863.
2. THE CORNER HOUSE LABORATORIES (PTY) LTD. Ref. 2794 and 3327. 1968.
3. CALTEAUX, R. J., NAUDE, D. E., and ROSSOUW, A. J. Report to the Transvaal and O.F.S. Chamber of Mines: On stream analysis of gold tailings solutions. Johannesburg, Chamber of Mines of South Africa, Ref. 507/67.
4. VAN DER MERWE, B., Metallurgical Research Officer, Blyvooruitzicht Gold Mining Co. Ltd. Private communication.

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