ON-LINE DETERMINATION OF SULFATE AND LIQUID DENSITY IN THE OXY HEMIHYDRATE^{tm} PROCESS

by
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ABSTRACT

Occidental Chemical Company (Oxy) has developed an integrated system for on-line determination of sulfate and density in filtered samples of phosphoric acid slurry. The system was developed with the support of Ionics, Inc. as an enhancement to the Oxy Hemihydrate™ Process. It consists of:

1. A proprietary Oxy sample vessel/filter holder.
2. A Marchon (Albright & Wilson, Ltd.) filter leaf.
3. A Marchon filtration/backwash controller,
4. An Ionics DigiChem 3000 programmable analyzer, configured for turbidimetric sulfate analysis
5. A proprietary Oxy Archimedean densimeter.

Features of the system include automatic self-calibration and self-cleaning each analytical cycle (12 minutes), 4-20 ma continuous signal output, and NEMA 4X enclosure. A plant test has shown accuracies within ±0.01 density units and ±0.15 sulfate percentage points over the ranges of interest.

INTRODUCTION:

In the manufacture of phosphoric acid from fluorapatite concentrate by various wet processes, such as the Oxy Hemihydrate™ Process, repeated measurements of the phosphoric acid sulfate concentration and liquid density are necessary for process control. Industry-wide attempts to mechanize or automate the measurement of these variables have met with limited success, and manual measurement methods still predominate.

Measurement of the density of the liquid phase of the phosphoric acid/calcium sulfate slurry is ordinarily accomplished by gravimetric or hydrometer determination on manually filtered samples. Several manual methods are in use for sulfate analysis.

Recently P. K. Bhattacharjee and B. L. Winslow* reported their experience at Agrico measuring sulfate concentration on-line by means of the Marchon (Albright & Wilson, Ltd.) sampler/analyzer system. The Marchon analyzer measures the turbidity of a $BaSO_4$ precipitate that forms when $BaCl_2$ is added to a filtered and diluted acid sample. The Agrico investigators report a requirement to clean and restandardize the instrument once per 8-hour shift to avoid drift. Occidental's experience with the Marchon analyzer/sampler is similar. Occidental has found the Marchon analyzers useful in showing sulfate trends, but unreliable for determination of absolute sulfate concentration.

Occidental has developed an integrated on-line automatic system for determination of sulfate and density in filtered samples of phosphoric acid slurry that overcomes drifting problems by avoiding the use of peristaltic pumps and incorporating automatic backwashing and calibration procedures. The sulfate analyzer is self-calibrating. The system was developed with the support of Ionics, Inc. as an enhancement to the Oxy Hemihydrate™ Process. This paper presents the results of a 4-day successful plant test carried out in February, 1986.

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* P. K. Bhattacharjee & B. L. Winslow, "Experience with On-Line Sulfate Analyzer" Presented at 190th ACS National Meeting, September 1985.

ON LINE ANALYZER SYSTEM CAPABILITITES

An analyzer system has been developed to provide automatic, reliable, and frequent determinations of sulfate and density for the liquid acid phase of the reaction slurry from the OXY Hemihydrate™ Process. The permanent installation of this system is expected to lead to better process control.

The system filters a sample of phosphoric acid/calcium sulfate slurry from a point in the process stream that is under positive pressure, then transfers the filtrate sample, in turn, to the sulfate analyzer and density meter. Sample lines are backwashed with water or EDTA solution to prevent scale accumulation. The sulfate analyzer is self-calibrating to correct for changes in response. The Ionics DigiChem Analyzer microprocessor controls sampling, analysis, autocalibration and transmission of results to the control room.

Details of the the system configuration, operation and results of testing are presented below:

EQUIPMENT CONFIGURATION

Figure 1 shows the arrangement of the four main components of the Oxy sulfate/density analytical system. The system consists of:

1. A proprietary Oxy sample-vessel/filter-holder.
2. A Marchon filter leaf.
3. A modified Marchon filtration/backwash controller,
4. An Ionics DigiChem 3000 programmable analyzer, configured for turbidimetric sulfate analysis
5. A proprietary Oxy Archimedean densimeter.

EQUIPMENT ITEM DESCRIPTION

1. The sample-vessel / filter-holder is a proprietary Oxy design for sampling slurry out of a process pipe that is under positive pressure. Features include:
   - A. Provision for shutting down the sample flow, isolating the sample vessel, then restarting, all while the main process line is operating.
   - B. Design so that one person can change the filter cloth in 5 minutes.
   - C. A design to minimize plugging and scaling. If a pluggage does occur, it may ordinarily be cleared without dismantling the equipment.
2. The Marchon filter leaf is commercially available, 6" diameter, grooved, and fitted with woven polypropylene filter cloth. Backwashing each cycle keeps the filter-leaf and cloth clean.
3. The essence of the Marchon filtration/backwash controller is an air-operated tubing pinch-valve that cycles between two positions: a filtration mode and a backwash mode. The operation of the valve is controlled automatically by the DigiChem analyzer. In the filtration mode, a filtrate stream from the filter leaf flows through a 100 cc sample collection cylinder, while a sample line leading to the analyzer is purged with water immediatly followed by air. In the backwash mode, water is forced back through the line to the filter, dislodging the filter cake, while the filtrate sample is pneumatically transferred from the sample cylinder to the DigiChem analyzer.

4. The Ionics DigiChem 3000 Analyzer automatically performs a batch turbidimetric sulfate analysis on a filtrate sample once every 12 minutes. The hybrid model at Occidental may be converted from a sulfate analyzer to a calcium analyzer in about 15 minutes. Its microprocessor contains a field-programmable RAM and a factory programmable ROM. The sulfate analytical cycle includes the following steps:

   - A two-position shuttle-valve catches a 1 cc acid sample, then shifts position to allow a metering pump to sweep the sample into the spin-cell with a known volume of "chaser" (dilute HCl & H_3PO_4).
   - A syringe with a piston driven by a high precision stepping motor withdraws an aliquot of the diluted sample from the spin cell.
   - The spin-cell is emptied and rinsed, then the sample aliquot is transferred back to the spin-cell for additional dilution.
   - Another syringe adds BaCl2 solution to the spin cell.
   - After a 1 minute reaction period, the turbidity of the resulting BaSO4 precipitate is measured by a photo-detector cell, and the resulting electrical signal is digitized and mathematically transformed into a sulfate concentration reading.
   - The spin-cell and internal sample line are flushed with EDTA, rinsed with deionized water, and reset for the next sample.

Features of the sulfate analysis program include:

A. 12 minute analytical/backwash cycle.

B. Reversion to backwash if plant pump shuts down.

C. Programmed rinsing & flushing.

D. Any of three calibration modes may be selected:

   1). attended, manually initiated.
   2). unattended, manually initiated.
   3). unattended, once every 'n' analyses, automatic.

The program for automatic calibration involves analyzing a known standard sample twice (at two different dilutions), then calculating the slope and intercept of the response. Figure 2 shows that the response on logarithmic coordinates of w/v% sulfate vs. sensor voltage is linear over the range 1.5 to 6% SO_4.

5. An Oxy Archimedean Densimeter, mounted in the DigiChem cabinet and under control of the DigiChem microprocessor, measures the density of the remaining acid sample discharged from the DigiChem shuttle valve within several seconds. The densimeter operates on Archimedes principle that bouyant force on a submerged object equals the weight of displaced fluid. Design of the densimeter is proprietary. Several features of the device include:

A. Low sample volume requirement (about 50cc).
B. Small overall size (about 20 cm x 10 cm x 10 cm)
C. Linear response with density.
D. Automatic DigiChem-controlled flush-cycle.

TEST RESULTS

After a series of shake-down tests and minor modifications, the analyzer system was tested around the clock for four days at Occidental's Swift Creek Hemihydrate Process™ plant. The system produced some very encouraging data.

Figure 3 shows that there was no significant drift in the DigiChem sulfate calibration during the week. This means there was no significant internal scaling or reagent degradation. Figure 4 shows the DigiChem sulfate analyses plotted along with the routine hourly operator sulfate analyses. Clearly the two results are consistent, and the average absolute deviation is ± 0.15 SO_4 percentage points. The calibration required no manual adjustment to give the results shown here.

Laboratory tests had shown the densimeter accuracy to be within ±0.001 g/cc. The densimeter ran the last 54 hours of the test without being manually cleaned or recalibrated. The programmed flush each cycle kept the unit nearly free of scale or sediment. Figure 5 shows the densimeter results along with routine hourly operator hydrometer measurements. It appears that if the densimeter had been recalibrated on hour #42 and again on hour #69, then the results would have matched those of the operator within ±0.01 g/cc. Bubbles or foam in the acid seem to affect results about one point in the second decimal place. Implementation of automatic recalibration of the densimeter seems feasible. The absence of temperature correction causes no appreciable problem as the sample temperature ordinarily varies less than ±5°C.

SYSTEM MAINTENANCE PROJECTION

The table below projects the system maintenance requirement based on plant-test experience:

		Period	Downtime
1.	Scheduled		
	A. Replenish reagent:	1 day	none
	B. Cloth change:	3 day	15 min.
	C. Replace soft tubing	1 wk	30 min.
	D. Recalibrate sulfate analyzer	1 wk	45 min
2.	Non-scheduled		
	A. Clear plugged sampler	plant upset	5 min
	B. Clear plugged tubing	1 day	10 min
	C. Replace soft tubing	2 day	15 min
	D. Clear plugged dispenser tip	1 wk	15 min
	E. Fix mechanical failure	2 wk	30 min

HARDWARE COST ESTIMATE:

The total hardware cost for the system described here is estimated to be about $50,000, 3/4 of that being the cost of the DigiChem Analyzer.

FUTURE PLANS

Future plans include programming an auto-calibration procedure for the densimeter, permanent installation of the SO_4/density analyzer system, plant-testing the on-line CaO analysis system, and eventual implementation of on-line control.

ACKNOWLEDGEMENT

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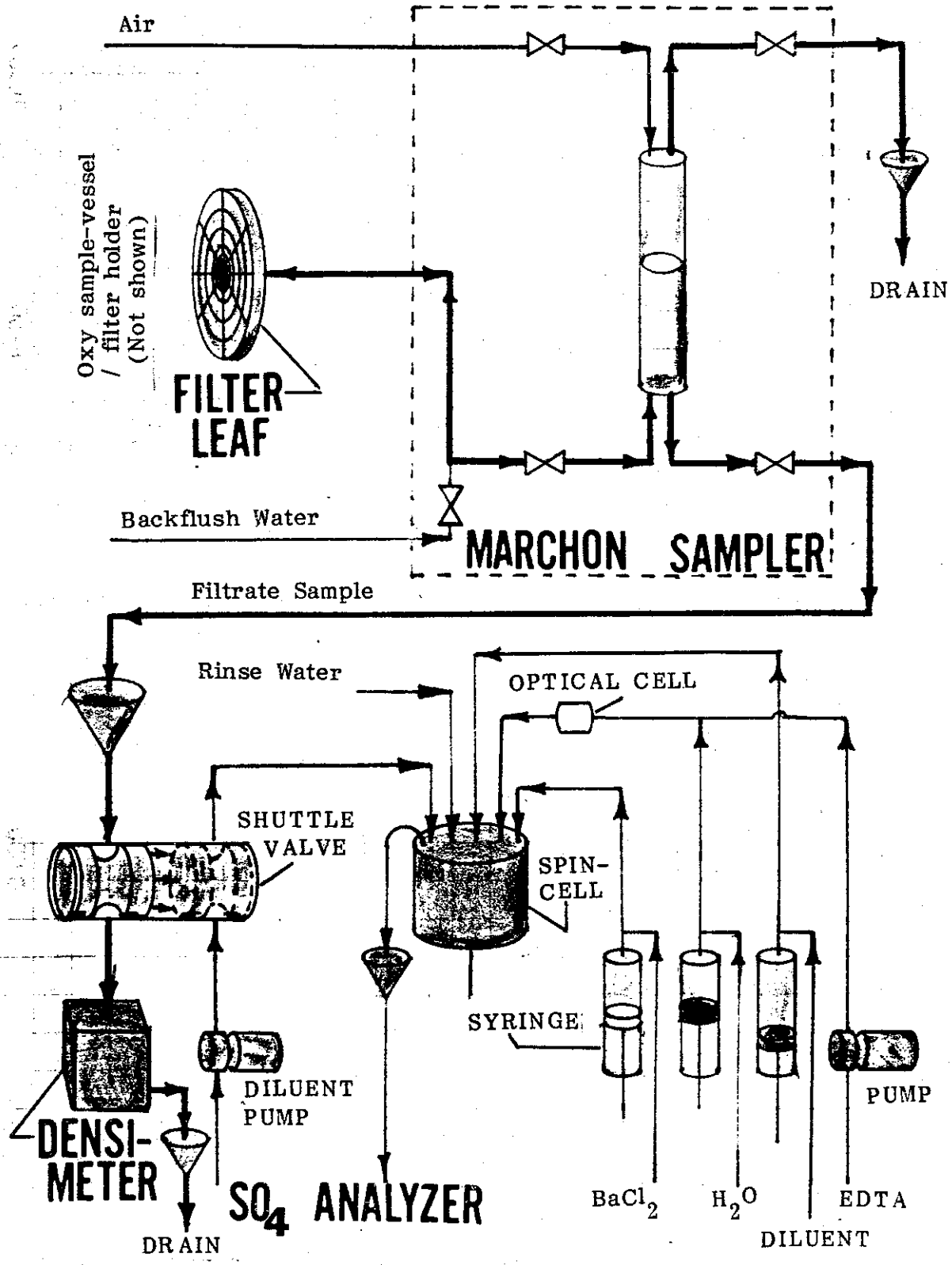

FIGURE 1 ANALYTICAL SYSTEM FOR SULFATE & LIQUID DENSITY

FIGURE 2 DIGICHEM RESPONSE

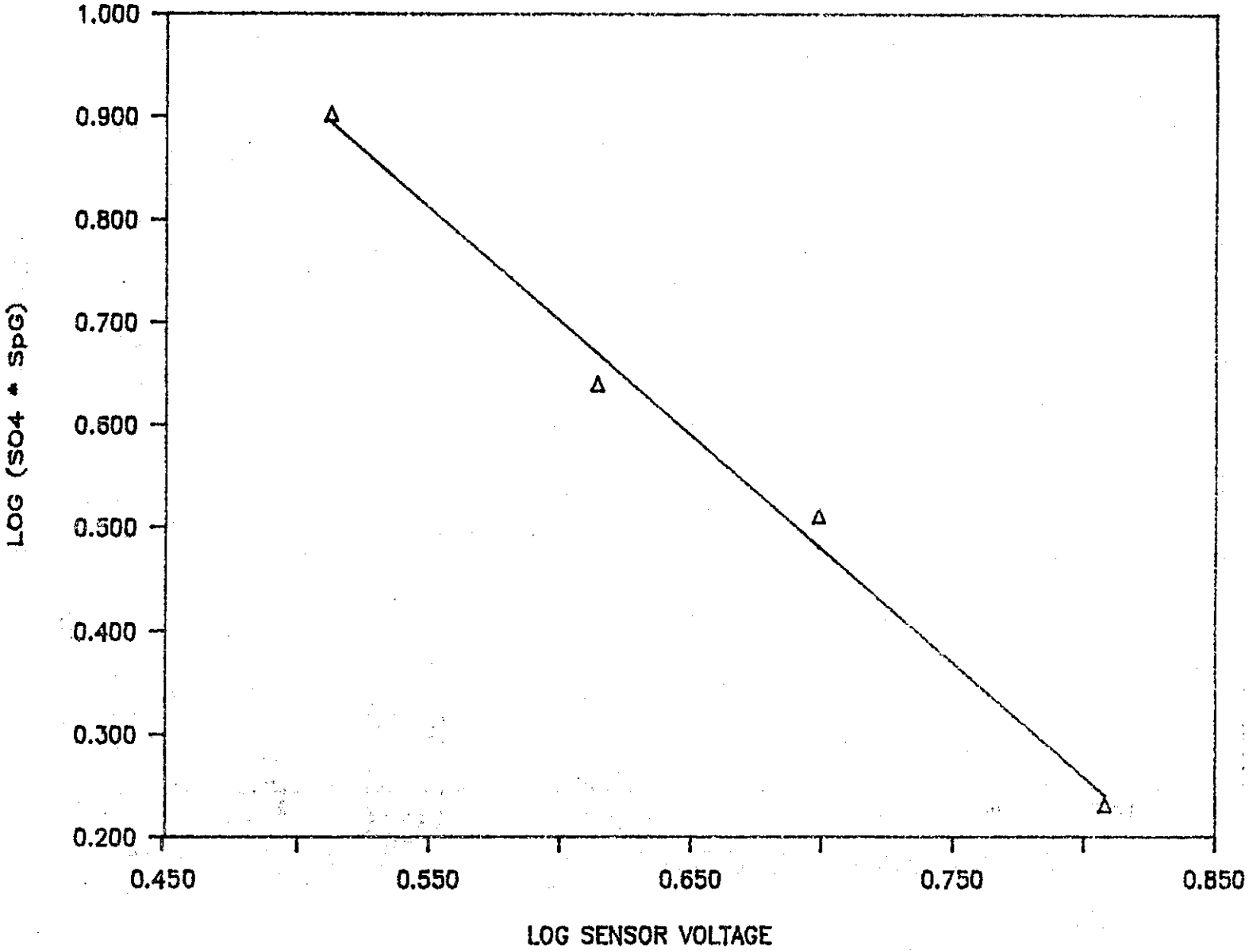

FIGURE 3 DIGICHEM CALIBRATIONS

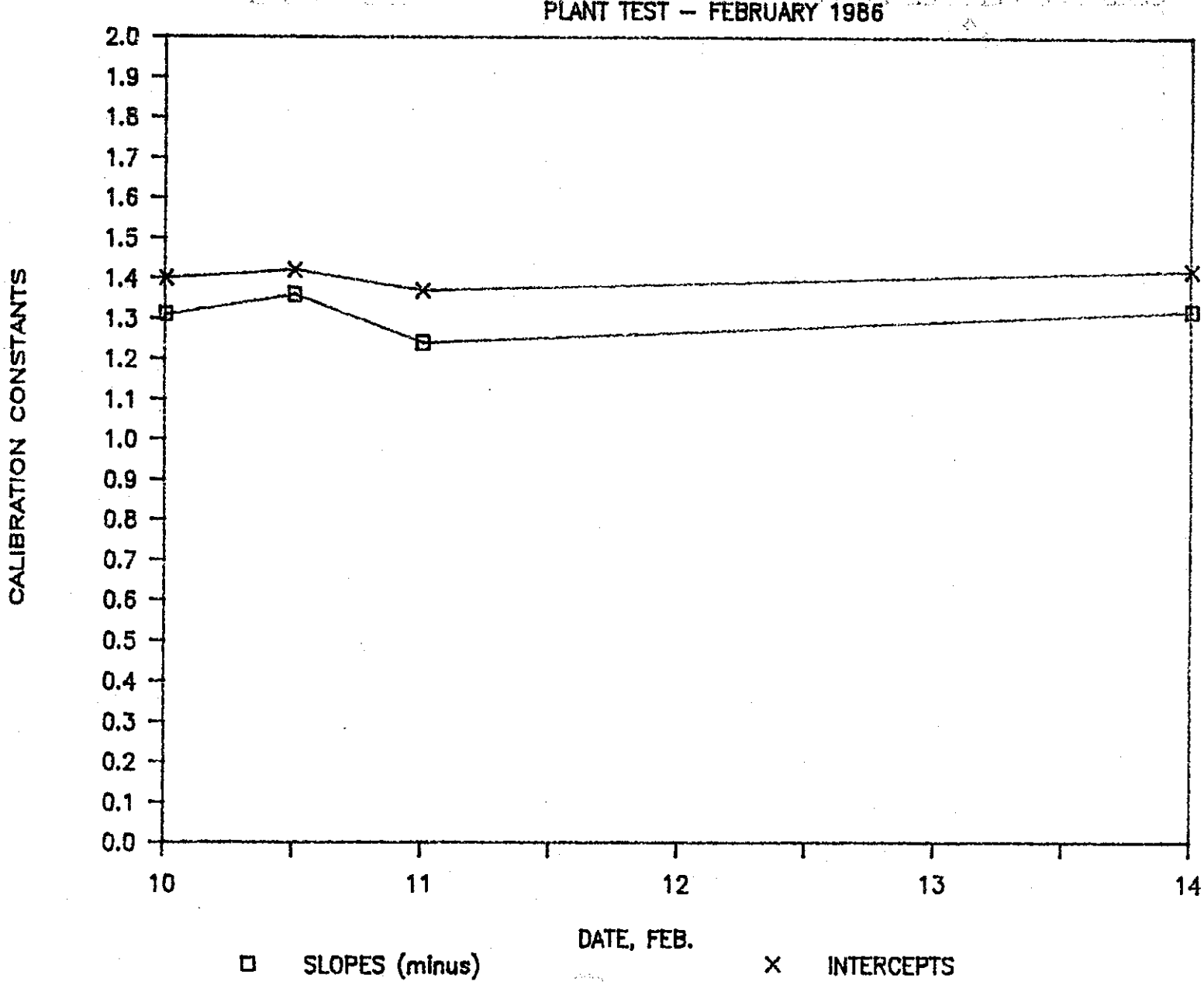

FIGURE 4 Sulfate Analyzer Plant Test

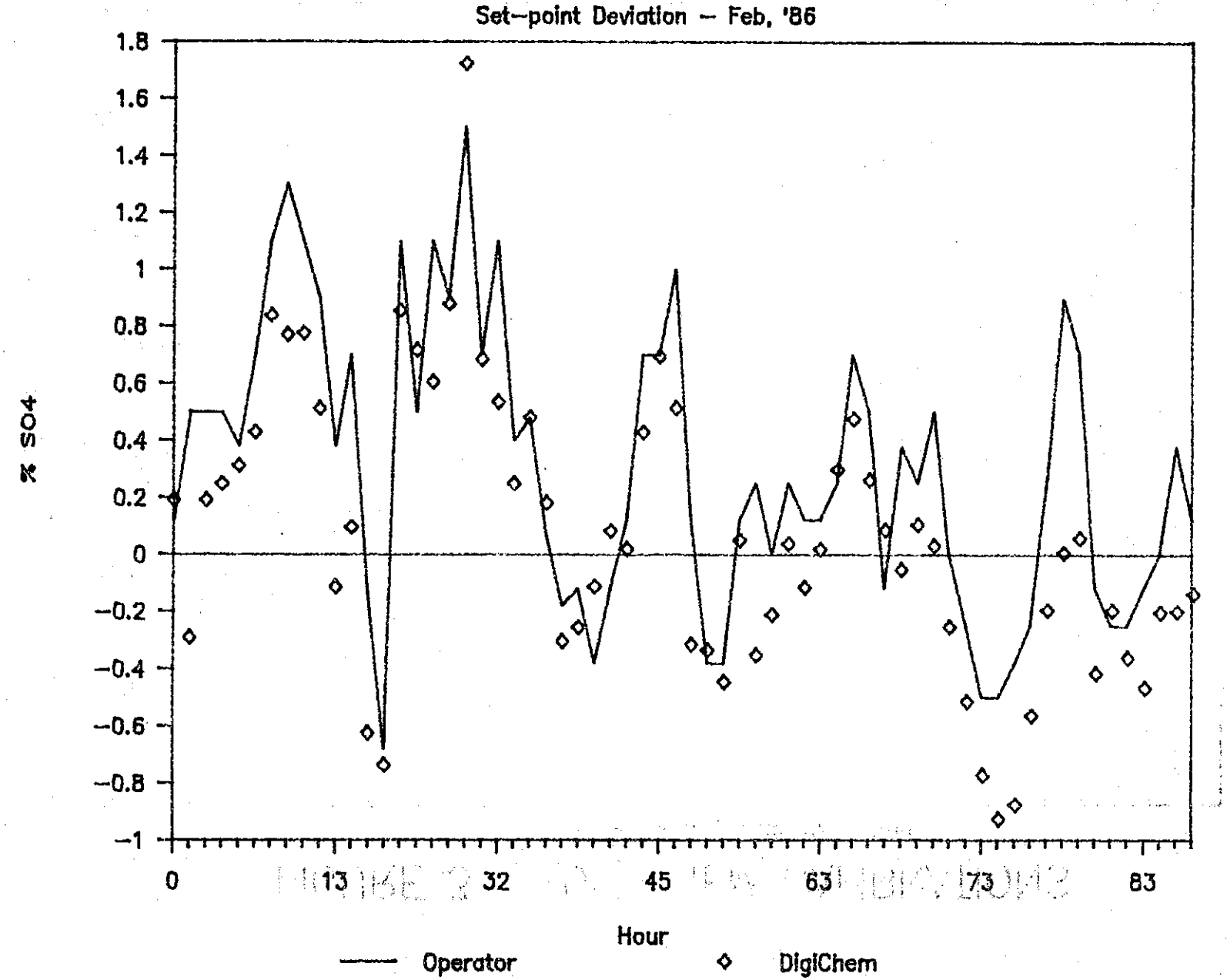

FIGURE 5 Density Meter Plant Test