AN EVALUATION OF HYDROXYLAMINE NITRATE MONITORING SYSTEMS

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LIST OF FIGURES

1. Effluent hydroxylamine composition
2. Sensor response
3. Electrodeless conductivity sensor
4. Pilot plant electrodeless conductivity response
5. Electrodeless conductivity response to hydroxylamine
6. Electrodeless conductivity sensor response to nitric acid
7. Sensor response during product elution
8. Cut-off prediction with conductivity
9. Potassium permanganate indicator system

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AN EVALUATION OF HYDROXYLAMINE NITRATE MONITORING SYSTEMS

R. D. Dierks

INTRODUCTION

A simple cation exchange process for converting hydroxylamine sulfate to hydroxylamine nitrate has been described by E. J. Wheelwright.⁽¹⁾ A proposal to construct a pilot plant utilizing this process has been described by L. E. Bruns and S. W. Swafford.⁽²⁾

An analytical instrument is needed to indicate continuously the composition of the effluent stream from this ion exchange column during the various steps of the processing cycle. This instrument is needed to enable operating personnel to gage exactly the times that the effluent stream should be switched to waste, recycle, or product receivers. The instrument would eliminate the need to estimate the switching times from flow rates and column capacities and then confirm these estimates by processing grab samples after the switching has been effected. The instrument is needed to minimize analytical costs, to realize a more uniform product, and possibly to enable the ion exchange cycle to be automated.

SUMMARY AND CONCLUSIONS

Electrodeless electrical conductivity, pH, oxidation-reduction potential (ORP), ultra violet absorption and chemical indicator techniques were investigated as possible methods for indicating the composition of the effluent stream from an ion exchange column producing hydroxylamine nitrate from hydroxylamine sulfate.

While pH measurements were more sensitive to changes during the rinsing cycle than electrodeless conductivity measurements and clearly showed the gradual removal of acidic materials during the rinsing cycle, the lack of detail during the elution cycle limited the investigation of pH to the preliminary measurements.

1. E. J. Wheelwright. "Cation-Exchange Conversion of Hydroxylamine Sulfate to Hydroxylamine Nitrate," BNWL-CC-2180, May 26, 1969.
2. L. E. Bruns and S. W. Swafford. "Hydroxylamine Nitrate from Hydroxylamine Sulfate," ARH-1309, July 3, 1969.

Preliminary ORP and pH measurements were not sufficiently different to warrant further investigation of ORP techniques. Ultra violet absorption measurements were not sufficiently informative to warrant anything other than preliminary measurements.

Electrodeless conductivity measurements were made in more detail and offer the following advantages.

1. Sensitivity to changes are equal to that of pH measurements, except in the very low concentration ranges such as are experienced during the rinsing of the loaded resin.
2. Sensitivity to changes during the product elution period are greater than those of pH measurement.
3. No contact is required with the process stream, minimizing sealing designs and process leakage.
4. There are no periodic standardization procedures required that introduce foreign materials into the process system.
5. There are no electrodes that require periodic replacement. The sensor is an all solid state, rugged device.

Chemical indication using potassium permanganate as an indicator was clearly the most accurate method of indicating low concentrations of hydroxylamine, particularly at the product cut-off point, however, the complexity of the system, the somewhat subjective judgment of color intensity required for indicator interpretation, the tendency of the equipment to plug with manganese dioxide and the hazard associated with the proximity of large amounts of permanganate and hydroxylamine, limited the investigation of this technique. If it is found necessary to pursue this technique further, the possibility of relating the temperature rise of the permanganate/effluent mixture to hydroxylamine content should be investigated.

DISCUSSION

Laboratory Studies

Some of the scouting studies for the ion exchange process for converting

hydroxylamine sulfate to hydroxylamine nitrate were carried out in a 1-inch I.D. glass column. During one of these runs, the effluent from the column was collected in seventy, 100 ml fractions. Each fraction was homogenized and analyzed for hydroxylamine, free nitric acid, and sulfate ion. The results shown in Figure 1 are typical of the operation of the ion exchange process and are characterized by the portions of Figure 1 labeled phase 1, 2, 3, 4 and 5. During phase 1, hydroxylamine sulfate solution is pumped into the column to affect absorption of the hydroxylamine by the ion exchange resin and rejection of the sulfate as dilute sulfuric acid. As the resin becomes loaded, the hydroxylamine sulfate passes through the column and appears in the effluent unchanged, typified by phase 2. During phase 3, the loaded resin is washed with distilled water, removing the unabsorbed hydroxylamine sulfate and the non-absorbable sulfate ion. Nitric acid is used to elute the hydroxylamine from the resin, as the nitrate, in phase 4 and return the resin to its hydrogen form. During the product elution phase, hydrogen ions work their way down the column and finally appear as an excess acid breakthrough as the hydroxylamine nitrate begins to tail off in the effluent. While this fifth phase is not apparent in Figure 1, it is readily seen in subsequent figures.

Conductivity, ORP and pH measurements of the effluent fractions are shown in Figure 2, and reflect clearly the sulfuric acid content of the effluent in phase 1 gradually shifting to hydroxylamine sulfate in phase 2. The gradual washing of the unabsorbed hydroxylamine sulfate and unabsorbable sulfate from the resin is seen in phase 3, with the pH measurement showing the greatest sensitivity to the changes occurring during this rinsing operation. The appearance of the hydroxylamine nitrate during phase 4, the elution period, is clearly indicated by all of the measurements, as is the breakthrough of the excess nitric acid eluant. None of the measurements show clearly the tailing-off of the hydroxylamine nitrate.

The ultra violet absorption spectra of samples typical of phases 3, 4 and 5 were compared with similar spectra for distilled water, hydroxylamine sulfate solution, 6N sulfuric acid and 1N nitric acid. The spectra were grouped closely about those for water, sulfuric acid and nitric acid, with the hydroxylamine content exerting an insignificant, if any, effect on the shape or position of the spectra.

Sodium dichromate and potassium permanganate solutions, used as self indicating titration reagents, were investigated for their possible use in a fixed sample/reagent ratio titrimeter. This titrimeter would simply indicate if the hydroxylamine content of the sample were greater than, or less than, some fixed value. The end point of the dichromate-hydroxylamine system was not sufficiently well defined to permit its use in such an instrument, however, the permanganate system exhibited a very sharp color change from purple to colorless with a very small change in the sample hydroxylamine content. By adjusting the permanganate concentration or the ratio of the permanganate and sample volumes used, a sharp color change was observed with approximately a 0.01M hydroxylamine concentration change, over the product cut-off range of interest of 0.05-0.4M hydroxylamine nitrate.

Pilot Plant Studies

Nine pilot plant demonstration runs of the ion exchange process were made using a 6-inch diameter ion exchange column. During these runs the column effluent line (1/2-inch polyethylene tubing) was fitted with the electrodeless, electrical conductivity sensor shown in Figure 3. Suitable electronics yielded a mv output signal and enabled the response of the sensor to be recorded on a mv recorder. The sensor and the electronics were designed and furnished by O. H. Koski of the Analytical Chemistry and Instrumentation Section.

Figure 4 is a facsimile of a typical record of the response of the instrument during the course of a demonstration run. As in Figure 2, the sensor shows the loading period clearly, however, since the feed contained only 12% hydroxylamine in excess of the quantity needed to saturate the resin bed, the indication of the hydroxylamine sulfate in phase 2 was limited to a slight inflection during the transition from loading to rinsing. Again, as in Figure 2, the response of the conductivity sensor is flat during the rinsing cycle although pH measurements indicate a steadily decreasing hydrogen ion concentration during this period.

The appearance of the product during the elution period, was very clearly and sharply indicated by the conductivity sensor. Figure 5 shows the response of the conductivity sensor as a function of the hydroxylamine nitrate concentration. The lower detection limit of the sensor is a function of the sensitivity of the recorder and the noise on the output signal. A multi-range instrument was used to record the response of the conductivity sensor during these demonstration runs, and on the 0-200 mv scale, signal noise was about 1% of the scale, equivalent to about .01M hydroxylamine. Thus, the lower detection limit for this system was approximately 0.02-0.03M hydroxylamine nitrate.

The appearance of the nitric acid eluant during the last half of the product elution phase, is also very clearly seen in the conductivity sensor response of Figure 4. Figure 6 shows the response of the conductivity sensor as a function of nitric acid concentration and Figure 7 shows the composite effect of these two components during the product elution phase.

Since the concentration of excess acid in the product is very critical, a knowledge of the hydroxylamine nitrate and the nitric acid in the effluent is vital in the determination of the point at which the effluent should be switched from a product receiver to a recycle or a waste receiver. Again, Figure 7 shows the typical overlap of the hydroxylamine nitrate and nitric acid as the product elution tails off, and the typical cut-off point for product collection. Figure 8 shows the relationship between the conductivity sensor and the hydroxylamine concentration at the cut-off point for seven of the pilot plant runs. From this it is seen that if the run conditions are maintained constant, the conductivity sensor can be used to accurately gage the cut-off point for either manual or automatic operation.

Permanganate Indication

To test the effectiveness of a potassium permanganate solution to indicate the concentrations of hydroxylamine in the effluent stream, two positive displacement pumps were assembled as shown in Figure 9. The pumps, Beckman Model 74602 Solution Metering Pumps, were variable stroke,

constant speed, piston pumps. Both pumps were adjusted to deliver 5 ml/min and were synchronized to give a simultaneous delivery of solution into a transparent sight glass. To minimize delay times, the suction and discharge piping to the pumps was made of 1/8 saran tubing of minimum length.

The permanganate indicator worked quite well, with the sight glass showing the dark purple color of the permanganate solution when the hydroxylamine concentration was low, and colorless when the hydroxylamine concentration was above about 0.25M. While the appearance of the excess hydroxylamine sulfate between the loading and rinsing phases showed only as an inflection in the response of the conductivity sensor, the permanganate indicator indicated a greater-than 0.25M concentration of hydroxylamine in the effluent all during this transition period.

No composition change was indicated either by the conductivity sensor or the permanganate indicator during the rinsing cycle.

The permanganate indicator responded to the product elution by the contents of the sight glass changing from the purple permanganate color to a water white solution. During this period it was noted that considerable heat was evolved in the reaction between the permanganate and the hydroxylamine and speculated that possibly the change in the temperature of the column effluent solution and the sight glass contents might be a better indication of the concentration of the hydroxylamine in the effluent than the color indication.

The most significant quality of the permanganate indicator is its ability to indicate the cut-off point of the product, in that the reaction between the permanganate and the hydroxylamine is little effected by the presence of the excess acid. During the tailing-off of the hydroxylamine in the elution phase, the reaction between the permanganate and the hydroxylamine of the sample slowly subsided in violence, the temperature of the sight glass decreased, and the color of the contents of the sight glass shifted slowly from water white to pink and finally to purple.

By shifting the concentration of the permanganate solution used by the indicator, or by changing the ratio of the pumping rates of the two

solutions, the hydroxylamine concentration at which the sight glass contents changed color could be adjusted to match the desired cut-off requirements.

In addition to the somewhat subjective judgement of color intensity required in the interpretation of this kind of indicator, this system has two other faults. One is the tendency of the system to plug solidly with manganese dioxide, precipitated during periods of low hydroxylamine concentrations, which results in either no flow of sample thru the system or an appreciable delay in the indication of increasing hydroxylamine concentrations. Second is the potential hazard of combining large quantities of permanganate and hydroxylamine thru equipment malfunction or operator error, which could result in a disastrous explosion.

FIGURE 1. EFFLUENT HYDROXYLAMINE COMPOSITION

FIGURE 2. SENSOR RESPONSE

FIGURE 3. ELECTRODELESS CONDUCTIVITY SENSOR

FIGURE 4. PILOT PLANT ELECTRODELESS CONDUCTIVITY RESPONSE

FIGURE 5. ELECTRODELESS CONDUCTIVITY SENSOR RESPONSE TO NH_2OH

FIGURE 6. ELECTRODELESS CONDUCTIVITY SENSOR RESPONSE TO HNO_3

FIGURE 7. SENSOR RESPONSE DURING PRODUCT ELUTION

FIGURE 8. CUT-OFF PREDICTION WITH CONDUCTIVITY

FIGURE 9. POTASSIUM PERMANGANATE INDICATOR SYSTEM