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Woo K. Park[a]; Edward D. Michaels[a]
[a] EG&G Mound Applied Technologies, Inc., Miamisburg, Ohio

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DISPLACEMENT BAND CHROMATOGRAPHY OF HYDROGEN SULFITES FOR ENRICHMENT OF SULFUR ISOTOPES

Woo K. Park and Edward D. Michaels
EG&G Mound Applied Technologies, Inc.*
Miamisburg, Ohio 45343

ABSTRACT

Experimental studies were conducted on the enrichment of sulfur isotopes by displacement band chromatography. In these studies, a band of hydrogen sulfite (bisulfite) ions from a sulfurous acid or bisulfite-salt solution was continuously displaced by bisulfate ions from a sulfuric acid or bisulfate-salt solution in a column packed with aminated polystyrene-divinyl benzene resin under varied process conditions. The sulfur isotopes were enriched through isotopic exchange between the bisulfite ions on the resin and the sulfurous acid and/or bisulfite-salt solution in contact with the resin within the moving band. During the isotopic exchange, S-34 isotope was favored in the resin phase and S-32 isotope in the liquid phase. As a result, the S-34 isotope was gradually enriched at the rear of the band, and S-32 isotope at the front. The effects of the various process conditions were evaluated on separative power, height equivalent to a theoretical plate, and operational simplicity. The highest separative power, 3.05 g S-34/cm^3/yr, was achieved with an ammonium bisulfite feed displaced by a sulfuric acid displacer at 65°C operating temperature.

INTRODUCTION

The chromatographic method had been successfully applied to the separation of sulfur isotopes (1,2,3). Recently this separation technique was re-examined by using the small-sized, high-performance resins that are currently available (4). A series of tests were conducted employing the experimental system that facilitated the

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displacement band chromatography (DBC). In the DBC a band of feed, containing the naturally abundant mixture of sulfur isotopes, was continuously displaced for isotopic separation through a column packed with an anion exchange resin. The tests confirmed the technical feasibility of the process along with its shortcomings:

- The need of a back-pressure to suppress SO_2 to keep it from bubbling,
- The swelling of the resin bed in contact with acid solutions, and
- The over-all low separative power.

The subsequent tests were, therefore, conducted to find the effects of some of the key process conditions that can be adjusted to improve the separation of sulfur isotopes.

EXPERIMENTAL

The experimental system was designed to form and drive a feed band in a column as previously reported (4). The column consisted of a glass tube, 6.3 mm i.d. and 33 cm long, fitted with two adjustable-length bed supports. The column was packed with an aminated, polystyrene-divinyl benzene, polymer resin (10 μ dia., 4% cross-linked, Benson BA-X4).

A feed solution was delivered to the column through a two-position switching valve. The feed band thus formed was driven through the system by a displacer solution, while a metering pump regulated the flow rate. To locate the band, the column effluent was monitored by the in-line pH and conductivity meters. Samples of the band were then collected on a fraction collector for mass spectrometer analysis. A more detailed account of the experimental system and procedure was reported elsewhere (4,5).

In the experimental system, tests were conducted at varied process conditions. For specific experimental purposes, the following were altered:

- The feed type (bisulfite-salts and sulfurous acid),
- The displacer type (bisulfate-salts and sulfuric acid),

- The regenerant type (sodium hydroxide and phosphoric acid), and
- The operating temperature (25 - 65°C).

Figure 1 shows the process employed to separate sulfur isotopes. The figure shows three stages of ionic-forms of the resin bed in contact with three processing liquids:

1. H_2O flusher,
2. Bisulfite-salt or sulfurous acid feed, and
3. Bisulfate-salt or sulfuric acid displacer.

Not seen in this figure is the NaOH or H_3PO_4 regenerant that converts the resin to OH^- or $H_2PO_4^-$ form in the initial preparation step prior to deionized H_2O flushing.

Figure 1 also indicates the formation and downward movement of a feed band by the continuous ion exchange reactions, driven by a displacer solution. It is this downward movement that promotes the counter-current flow of the ions of the resin phase and the solution of the liquid phase within the band and that induces the development of an axial isotopic concentration profile through isotopic exchange reactions between two phases.

The following are the typical reactions that take place at different parts of the band:

At the front boundary of the band,

$$OH^--R' + H_2SO_3 = HSO_3^--R' + H_2O \qquad (1)$$

where -R′ denotes resin phase and H_2SO_3 aqueous SO_2.

Within the band,

$$H^{32}SO_3^--R' + H_2{}^{34}SO_3 = H^{34}SO_3^--R' + H_2{}^{32}SO_3 \qquad (2)$$

At the rear boundary of the band,

$$HSO_3^--R' + H_2SO_4 = HSO_4^--R' + H_2SO_3 \qquad (3)$$

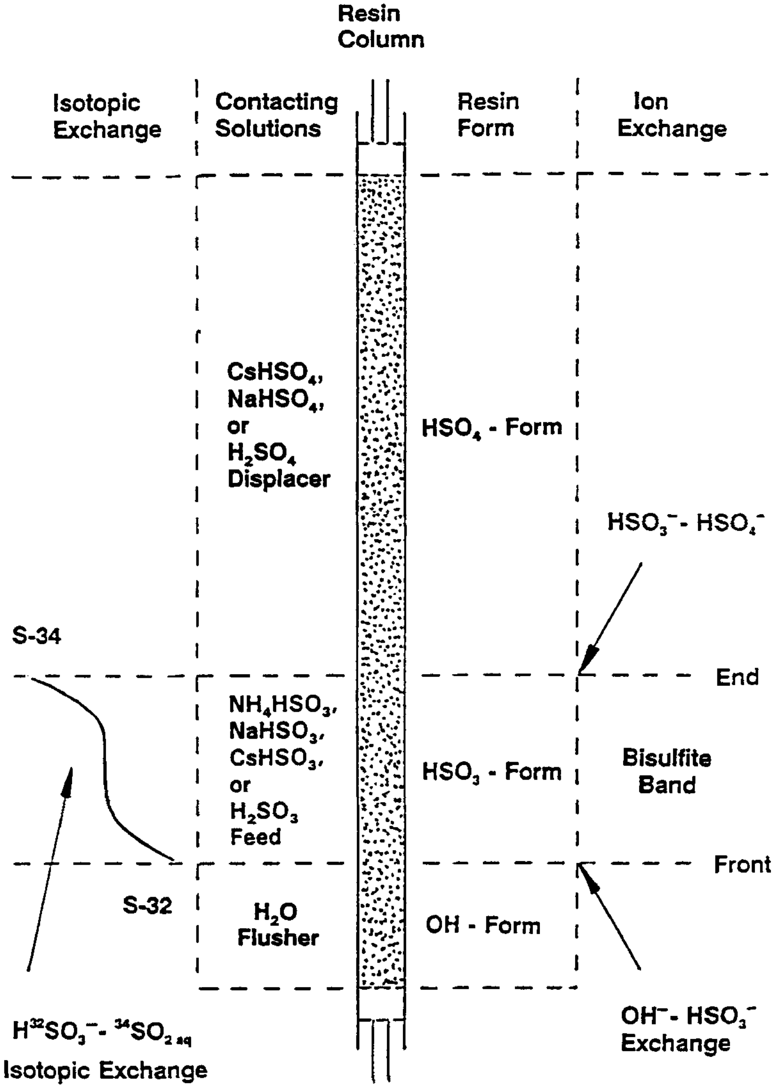

FIGURE 1. Separation scheme for sulfur isotopes.

RESULTS AND DISCUSSION

As reported in the other paper (4), the actual physico-chemical behavior of the band was more complex than that categorically described in the previous section. It was, therefore, anticipated that the data calculated under the assumption of idealistic DBC would not precisely represent the real situation. However, no effort was made to determine the extent of possible deviation since it was considered insignificant for the short column tests conducted in this work. Furthermore, the scope of the work was confined to finding the general effects of common process variables on the sulfur isotope separation by using a computerized calculation method.

The following process variables were chosen for these studies:

1. Type of cations contained in feed and displacer solutions,
2. Type of regenerants, and
3. Operating temperature.

The effects of these process variables were obtained by analyzing the test results in terms of separative power and HETP. Separative power defines the maximum attainable production rate of a desired isotope per unit volume of a cascade. HETP is the height equivalent to a theoretical plate. These terms were calculated by solving the following equation of continuity for isotopes:

$$M_b \frac{\partial x_i}{\partial t} = \frac{H_o}{Y_o} \frac{\partial^2 x_i}{\partial z^2} - H_o \frac{\partial}{\partial z} \left[x_i\left(d_i - \sum d_j x_j\right)\right] \qquad (4)$$

where x_i = mole fraction of i^{th} component
x_j = mole fraction of j^{th} component
M_b = band inventory, g
H_o = $\epsilon_o B$, initial transport coefficient per unit mass difference, g/s
Y_o = $\epsilon_o n$, dimensionless stage number per unit mass difference
ϵ_o = separation coefficient for unit mass difference (typically 0.005)
d_i = $m_i - m_n$, mass difference of i^{th} component relative to n^{th} component, g

$d_j = m_j - m_n$, mass difference of j^{th} component relative to n^{th} component, g

z = normalized length, cm

t = time, s

After this equation was numerically solved, the result was fitted to the isotopic concentration profile obtained experimentally. Then the HETP value,

$$\mathrm{HETP} = \epsilon_o L_b / Y_o \tag{5}$$

was calculated with the measured band length, L_b.
Similarly, the separative power was calculated by using the defining equation,

$$\delta U = H_o Y_o / (4 L_b A) \tag{6}$$

where A is the cross-sectional area of the resin column.

Effects of Cations

Two types of feeds, sulfurous acid (H_2SO_3) and bisulfite-salts (e.g., NH_4HSO_3, $NaHSO_3$ and $CsHSO_3$) were tested to find the comparable effects of the cations (NH_4^+, Na^+ or Cs^+) in the feed on the process and its outcome. When a feed solution was admitted to the anion-resin column, the bulk of cations ionized from the feed was separated from the anionic bisulfite adsorption band and carried along the column far ahead of the band. The cations from the bisulfite-salt feeds were monitored as they left the column by a conductivity detector. However, a small amount of cations were, presumably, not carried away with the bulk, and these remaining cations might have affected the physico-chemical nature of the band for the better. It appears that absorption of SO_2 was enhanced by these cations to the extent that the feed band formed from a bisulfite-salt was stable even at an atmospheric pressure. A high back-pressure (e.g., 200 psi) typically required to keep SO_2 from bubbling, as in the band formed from a H_2SO_3 feed, was not necessary when processing a bisulfite-salt feed.

Besides the stabilization of the band, no other significant effects were induced by the cations of the bisulfite-salt feeds. The length and velocity of the bands were about the same for all three

TABLE 1. THE CONDITIONS AND RESULTS OF SELECTED CHROMATOGRAPHIC TEST RUNS*

Run #	Regenerant M	Feed mL x M	Displacer M	Temp. °C	Sep. Power $g/cm^3/yr$	HETP cm
49	H_3PO_4 1.0	H_2SO_3 1.5 x 0.97	H_2SO_4 0.35	65	1.62	0.021
50	NaOH 1.0	$NaHSO_3$ 1.5 x 0.97	H_2SO_4 0.35	25	1.23	0.021
51	NaOH 1.0	NH_4HSO_3 1.5 x 0.97	H_2SO_4 0.35	25	1.59	0.025
53	NaOH 1.0	NH_4HSO_3 5.0 x 0.5	H_2SO_4 0.35	65	3.05	0.013
56	NaOH 1.0	NH_4HSO_3 2.5 x 0.6	$NaHSO_4$ 0.60	65	0.87	0.026
61	NaOH 1.0	$CsHSO_3$ 3.0 x 0.5	$CsHSO_4$ 0.35	25	0.70	0.021
62	H_3PO_4 1.0	H_2SO_3 1.5 x 0.97	H_2SO_4 0.35	25	1.16	0.033

* Resin = 10 μm diameter BA-X4; Flow Rate = 0.312 mL/min

feeds. Naturally, the separative power and HETP value were approximately the same.

The observed cation effects of bisulfite-salt feeds on the characteristics of the feed band became more apparent when a bisulfate-salt (e.g., $NaHSO_4$ or $CsHSO_4$) solution was used as a displacer instead of H_2SO_4. In such a process, the cations from a displacer continuously flowed through the feed band, subjecting the whole band, in essence, to the influence of steadily passing cations.

As expected, the SO_2 gas in the feed band did not bubble under this condition. However, the process formed an expanded band (up to 60% longer) with a wavy front boundary. The band's expansion seems to be a result of dispersing and diluting the feed due to the continuously fleeting cations.

In the run made with a $CsHSO_4$ displacer, even the band velocity was lowered, probably due to a lower concentration of HSO_4^- displacing ions in the solution because the solution has a lower degree of ionic dissociation.

As presented in Table 1, the separative power was lowered when the bisulfate-salt displacers were used, as in Runs No. 56 and 61, instead of H_2SO_4, as in Runs No. 50, 51 and 53. It appeared that the physico-chemical balances (including the separation factor) of isotopic exchange within the band were adversely affected by the continually passing cations (e.g., Na^+ or Cs^+). The S-34 concentration profiles obtained from Runs No. 56 and 61 reflected such effects with their flatly stretched shapes.

Effects of Regenerants

For most of the anion exchange resins, a NaOH solution was the most dependable regenerant that offered rapid ion exchange at reasonable operating conditions. However, some exceptional cases required a regenerant other than a NaOH. When the column packed with a 4% cross-linked resin was being operated with a H_2SO_3 feed at 25°C, the system pressure gradually increased above the mechanically allowable limit (e.g., 500 psi) after its regeneration with a NaOH solution. This problem with the system pressure was not encountered when the system was operated at a higher temperature (e.g., 65°C) or with a bisulfite-salt feed at any temperature, and it was not experienced with the column packed with a highly cross-linked resin (e.g., 8 or 12%) under any regenerant-feed-temperature conditions.

Since the high system pressure was quickly relieved as soon as the band front moved out of the column, the authors assumed the following:

- That the pressure build-up was caused by a gradual clogging, possibly with an insoluble material that accumulated at the front of the band or at the filter at the bottom of the column, and
- That the regenerant played a role in causing it.

Therefore, in an attempt to keep the pressure from building up, the authors tried an alternate regenerant, H_3PO_4, and obtained mixed results. No clogging occurred in the column, as evidenced by no apparent pressure build-up. However, the band was expanded (a maximum of 30%) with its irregular front. Somewhat poor ion exchange at the front of the band was ascertained from the resultant S-34 concentration profile that showed a rather leveled front half. The separative power was consequently lowered for the runs made with a H_3PO_4 regenerant (Runs No. 49 and 62), compared with those with a NaOH regenerant (Run No. 53 and those reported in Reference 4).

The effectiveness of the H_3PO_4 regenerant in limiting the swelling of the resin bed was also observed in the column packed with an Aminex resin. The problem of pressure build-up was severe in this column when it was operated after regeneration with a NaOH regenerant. As the feed and displacer solutions flowed through the column, the resin bed started swelling, eventually blocking the flow, and the system pressure increased above the operable limit. However, when the column was operated after regeneration with a H_3PO_4 solution, the swelling of the resin bed was greatly reduced and manageable with a reasonable build-up of pressure. All these results suggest that a H_3PO_4 regenerant may be used for the resins that have the tendency to swell excessively.

Effects of Temperature

In general, as the temperature of the resin column was increased, the boundaries of the feed band became sharper and the concentration profile for S-34 became more distinct. As a result, the HETP value was decreased and separative power increased. (See Run No. 62 vs. Run No. 49 and Run No. 51 vs. Run No. 53). Even the problem of high pressure build-up due to clogging was negligible at high temperatures. However, the band expanded (up to 41%) as the column temperature increased to 65°C, thus slightly nullifying the increase of the separative power. Such band expansion and its subsequent effect were also noticed in the runs made with a 12% cross-linked resin column (4). For those runs, some negative effects were, however, experienced at a high temperature. The separative power that was quite high (e.g., 3.9 g S-34 /cm^3/yr) even at 25°C was actually lowered at a high temperature due to the band's expansion (4). Yet, the highest separative power was achieved at 65°C in the 4% cross-linked resin column (Run No. 53) as shown in Table 1.

CONCLUSIONS

The enrichment of sulfur isotopes via displacement band chromatography can be enhanced by adjusting the process conditions to their optimum settings. The process conditions that adjust to increase the separative power of the system include the type of contacting solutions, as well as operating parameters. Among the regenerant solutions available for anionic resins, a NaOH solution provides the best regenerated condition for most resins. For the resins with excessive swelling or clogging problems, a H_3PO_4 solution can be used with some lowering of the separative power. An NH_4HSO_3 or $NaHSO_3$ feed has an advantage over H_2SO_3 in permitting operation at a lower pressure, probably at a slight expense of separative power. An H_2SO_4 displacer yields a higher separative power than bisulfate salts. To lower the pressure, one can choose to operate at a higher temperature (less than 65°C) without losing any separative power. In these experiments, when a 4% cross-linked resin was used, the separative power was higher. When a 12% cross-linked resin was used, the separative power was about the same.

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