

clean surface. Consequently, the comparison of the rate of evaporation for cases with and without monolayers on the basis of comparable wind velocities was actually obtained under quite different wind shear velocities. Since the wind shear velocity, rather than the wind velocity, is believed to be the governing parameter for evaporation, and since the difference in the wind shear velocity is great enough to account for the claimed reduction, I conjecture that the retardation of evaporation due to monolayers in the field under turbulent wind may actually be due to the wave-damping effects of these layers.

Note added in proof: A note (8) on the effect of the wave-suppressing characteristics of macromolecular films in retarding evaporation appeared after this report was submitted for review. The mechanism proposed herein is, nevertheless, entirely different from that suggested by Garrett. He considered that the wave suppression acts

to diminish the area of the water surface in contact with air. On the other hand, I consider that the wave suppression alters the wind structure. In other words, Garrett's interpretation is based on geometry, an area change of the air-water interface, whereas my interpretation is based on dynamics, a change of transport processes above the air-water interface.

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8 July 1971

Methyl Mercury and Inorganic Mercury Collection by a Selective Chelating Resin

Abstract. *A commercially available chelating resin selectively and quantitatively collects methyl mercuric and inorganic mercuric forms of mercury to the exclusion of all other metals studied, except the noble metals. Both forms of mercury can be collected from pH 1 to 9. Collected mercury is readily eluted with a slightly acid, 5 percent solution of thiourea, and the resin can be reused for many cycles. Selectivity, pH effects, capacity, and elution characteristics of the resin are described. A resin-loaded paper composed of 50 percent resin and 50 percent cellulose shows properties similar to those of the loose resin.*

The purpose of this report is to summarize available tests on a chelating resin, Ionac SRXL (1), which should provide new opportunities for analysis and for recovery of mercury from industrial and natural aqueous solutions. Previous studies have shown that the resin is highly selective for gold and platinum metals, but its usefulness for mercury had not been considered (2-4). My results indicate that the resin has a high affinity for dissolved mercury in both the methyl mercury and the inorganic forms.

Koster and Schmuckler, original developers of the resin (2), explain the selectivity for noble metals by stating that it will "... bind only ions with the d^8 electronic configuration forming square planar complexes. . . ." They further explain that the resin has redox properties because of double bonds, en-

abling it to collect a species such as Pt^{4+} which is reduced to the Pt^{2+} and then bound as a square planar complex. The mechanism for Hg^{2+} and CH_3Hg^+ collection has yet to be determined.

The properties of SRXL resin were studied in two ways. Data were obtained with resin as received from the manufacturer and with resin-loaded paper, consisting of 50 percent SRXL resin (-325 mesh) and 50 percent

cellulose (4). Comparisons were made between the resin behavior in a column and its behavior in the resin paper. All solutions were prepared with reagent-grade chemicals, and tracer studies were performed with the ^{203}Hg radioactive isotope and a NaI(Tl) detector.

Selective collection of noble metals, especially gold, from solutions containing high concentrations of more common metals has been reported (2-4). I have found also that the resin quantitatively collects dissolved mercury as methyl mercury or as inorganic mercury from solutions of high common metal concentration. A column of resin, 30 by 15 mm, quantitatively collected 100 μg of Hg^{2+} from 250 ml of chloride solutions of iron, nickel, copper, and zinc in amounts up to 10 g/liter. Radioactive ^{203}Hg was used to determine the completeness of collection (Table 1).

Selectivity tests for mercury in the CH_3HgCl , $HgCl_2$, and $Hg(NO_3)_2$ forms were conducted by filtering solutions containing a mercury salt mixed with various metals through paper disks (3.5 cm in diameter) containing SRXL resin; the solution was passed six times through each disk. The disks were rinsed with dilute HCl solution, dried, and analyzed by fluorescent x-ray spectrography. From solutions containing Fe^{3+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , and Hg^{2+} or CH_3Hg^+ , only the mercury was detected on the disks; the instrument conditions were sensitive to less than 5 μg for any one of the metals. Neutron activation analysis of SRXL paper disks which were used to collect gold from solutions containing nitrate or chloride salts of metals failed to show any common metal collection (4).

Comparisons with another resin, Chelex 100, reported to have a high affinity for Hg^{2+} , show that the Chelex 100 resin fails to collect the methyl mercury form although it does quantitatively collect Hg^{2+} . A paper specially prepared (H. Reeve Angel & Co.) with the Chelex 100 resin, was compared chromatographically with the SRXL

Table 1. Mercury ion (Hg^{2+}) collection from solutions of high metal concentration.

Conc. of Fe, Ni, Cu, and Zn mixture (g/liter)	^{203}Hg (count/min) *			Hg collected (%)
	Before	After	Background	
0.5	5202	217	224	~ 100
1.0	5318	214	213	~ 100
5.0	5498	225	209	~ 100
10.0	5510	225	209	~ 100

* Average of four or more 1-minute counts.

paper. Metal mixtures including Hg^{2+} and CH_3Hg^+ were placed on both papers and developed under identical conditions. The SRXL paper showed complete separation of all metals examined (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+}) from the Hg^{2+} and CH_3Hg^+ spot, which always had an R_F value of 0. The common metals showed no tendency to be retained by the paper. The Chelex 100 paper showed some affinity for most of the metals. Some spreading of the Hg^{2+} was also noticed. This comparison emphasizes the fact that the SRXL resin has the ability to discriminate between mercury and base metals instead of merely exhibiting varying degrees of affinity for the different ions as is more commonly observed in ion exchange.

The effect of pH on the collection of mercuric chloride, mercuric nitrate, and dissolved methyl mercury by the resin and the resin paper was examined over the pH range of 0.1 to 9. The results (Fig. 1) suggest the possibility of separating the forms of mercury in solution by pH adjustment. The trends and not the magnitudes are significant because different experimental procedures were necessary depending on whether the resin or the paper was used. Collection times were restricted to avoid quantitative collection as the purpose of this study was to observe differences in diffusion and absorption kinetics.

For the loose resin (Fig. 1A), a 200-ml solution, adjusted to the desired pH with dilute HCl and NaOH and containing ^{203}Hg radioactive tracer and 1000 μg of Hg^{2+} , or $\text{CH}_3^{203}\text{Hg}^+$ tracer and 990 μg of Hg as CH_3Hg^+ , was shaken with 0.33 g of resin on a mechanical shaker for 2 hours. Portions (3 ml) were taken for the determination of radioactivity before resin addition and after shaking, in each case, to determine the amount of mercury collected by the resin. Although mercury is collected at $\text{pH} > 7$, use of the resin is probably best confined to $\text{pH} < 7$ as recommended by Koster and Schmuckler (2). The lowest collection of inorganic mercury is at pH 6. One liter of a pH 6 solution containing ^{203}Hg tracer and 100 ppm of Hg^{2+} as the chloride was prepared and passed through a small column (1 by 1.5 cm; 0.75 g) of the resin. The effluent from the column was periodically checked for ^{203}Hg activity. After about 600 ml of the solution had passed through the resin at an initial flow rate of 3 ml/min, a small amount (about 2 percent) of

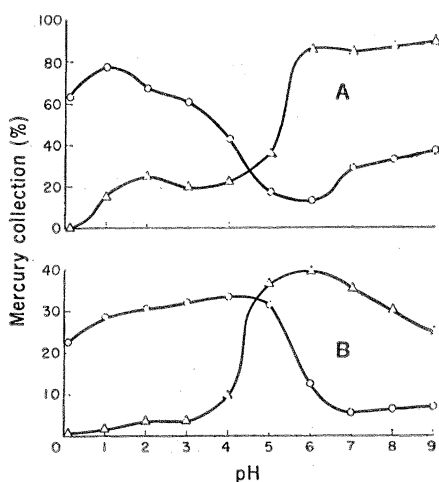


Fig. 1. Effect of pH on the collection of inorganic mercury (O) and dissolved methyl mercury (Δ), by SRXL resin (A) and SRXL resin-loaded paper (B).

mercury tracer began to come through the column. When the flow rate was reduced to approximately 1.5 ml/min, the mercury collection was again quantitative, and no further escape of mercury from the column was observed for the remainder of the 1000 ml of solution. These observations indicate that the total capacity of the resin is probably the same at pH 6 as at the lower pH values, but the rate of collection of Hg^{2+} is slower at pH 6. Therefore, a slower flow rate will be all that is required for quantitative recovery of inorganic mercury at this pH .

For the SRXL paper (Fig. 1B), small disks (1.3 cm in diameter) of the paper were suspended by thread for 24 hours in solutions of various pH , each solution containing 1000 μg of Hg as HgCl_2 or 930 μg of Hg as the methyl mercuric chloride. The disks were dried, and the mercury content was determined by fluorescent x-ray spectrography.

The sudden decrease in collection of the inorganic mercury at pH 6 is apparently the result of a reduction-precipitation reaction occurring on the surface of the suspended disks. The surface of the paper disk turns dark, and a white precipitate forms in the solution around the disk, suggesting the reduction of the Hg^{2+} to Hg^0 and Hg_2^{2+} followed by precipitation. An essentially identical curve of the effect of pH on behavior, with darkening of the disks and formation of a white precipitate, is also observed in the collection of $\text{Hg}(\text{NO}_3)_2$ from nitrate solutions containing no chlorides. Filtering solutions of pH 6 or greater through SRXL resin-loaded paper results in quantita-

tive recovery of the inorganic mercury. No precipitate formation or darkening of the disks was noticed in the solutions containing the methyl mercury.

The capacity of the SRXL resin for Hg^{2+} was determined by shaking 1-g portions of the resin with chloride solutions at pH 1.5 containing 2 g of HgCl_2 and 10 μc of ^{203}Hg . Portions were taken at intervals for the determination of radioactivity until no further loss of tracer from solution was observed. The capacity of the resin under these conditions was 540 to 550 mg of Hg^{2+} per gram of dry resin. This compares well with the 488 mg per gram of dry resin found by Koster and Schmuckler for Pt^{4+} (2).

A 5 percent aqueous solution of thiourea containing 5 ml of hydrochloric acid per liter will elute gold and platinum metals from the resin, permitting its reuse for many cycles (5), therefore this eluent was investigated for the removal of mercury from the SRXL resin. A series of eight cycles of mercury collection and elution were performed with the same 2-g portion of resin. For each cycle, mercury was collected from 100 ml of solution containing ^{203}Hg tracer, and each cycle contained the same amount or more mercury than the one preceding. The 100-ml volumes contained from 100 μg to 1 g of Hg . Tracer activity of 3-ml portions of each effluent showed that the collection was 100 percent at all concentrations. Mercury was then eluted from the resin with 10-ml portions of the 5 percent thiourea solution. More than 90 percent of the mercury was removed with the first 10 ml of eluent in each case, and elution was essentially complete after passing 30 ml through the resin. A rate of approximately 3 ml/min was used for the elution and the collection. After elution of the mercury, the excess thiourea was washed from the resin with distilled water, and the next 100 ml of solution were passed through the resin, starting the next cycle.

Thus the ability to selectively and quantitatively collect the highly toxic methyl mercury as well as inorganic mercuric salts, and the ability to be reused for many cycles, make this resin a very promising tool for attacking both the analytical and the industrial problems of mercury pollution.

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References and Notes

1. The SRXL resin, used to obtain the data for this report, is no longer commercially available from the Ionac Chemical Co., Birmingham, N.J. A resin reportedly identical is available from the Ayalon Water Conditioning Co., Ltd., P.O. Box 586, Haifa, Israel, under the trade designation of Srafin NMRR. Trade names and company names are used in this report for identification only and do not imply endorsement by the Bureau of Mines.
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Olivines: Revelation of Tracks of Charged Particles

Abstract. *A one-step, three-component aqueous etchant was developed for revealing the tracks of charged particles in olivine. The etchant reveals tracks of small cone angle, which are equally well developed in all the crystallographic directions. The scope of fossil cosmic-ray track studies in extraterrestrial samples has thus been increased, because olivine is often an abundant constituent and because it has a higher threshold ionization for track registration and has lower uranium, thorium, and trace element concentrations as compared with pyroxenes and feldspars. The etchant does not attack any of the principal rock-forming minerals in normal etching time, which allows a nondestructive study of fossil tracks in thin-section mounts. The study of fossil cosmic-ray tracks in olivine is particularly valuable for investigations of very, very heavy cosmic-ray nuclei and for highly irradiated samples such as those found in the lunar regolith.*

The existence of cosmic-ray and spontaneous fission records in meteoritic and terrestrial minerals has demonstrated the usefulness of these solid-state detectors for the study of the cosmic-ray prehistory, the age, and the thermal history of minerals (1). For most of the rock-forming minerals in terrestrial and extraterrestrial samples, a suitable acid or alkali etchant exists (2, 3). However, for olivine, $(\text{Mg,Fe})_2\text{-SiO}_4$, which is usually abundant in most extraterrestrial samples (4), no satisfactory etchant has yet been reported. It has been claimed that etching with KOH and HF reveals tracks on the (100) face (5). No informative data based on studies of the (100) face have yet been reported, since such studies are time-consuming and applicable only in limited cases when large crystals are available. In this report we describe an etchant for satisfactorily revealing tracks in olivine, regardless of the crystallographic orientation.

The etchant described here was developed after we had made systematic studies of the shapes of tracks and the extent of development in a large number of randomly oriented crystals, both for cosmic-ray tracks in meteoritic olivines and for fission-fragment tracks in terrestrial and meteoritic olivines. On the basis of such studies and also on the basis of the observation of the tracks revealed on a given crystallographic plane by different chemicals, we were

finally able to make up a compatible multicomponent etchant that showed little or no preference between different crystallographic directions in the revealing of tracks. The results of this study are discussed in detail elsewhere (6); the salient features of the olivine etch, designated as "WN," are described here.

The WN etchant is prepared by successively mixing 1 g of oxalic acid, 1 ml of orthophosphoric acid (85 percent), and 40 g of the disodium salt of EDTA

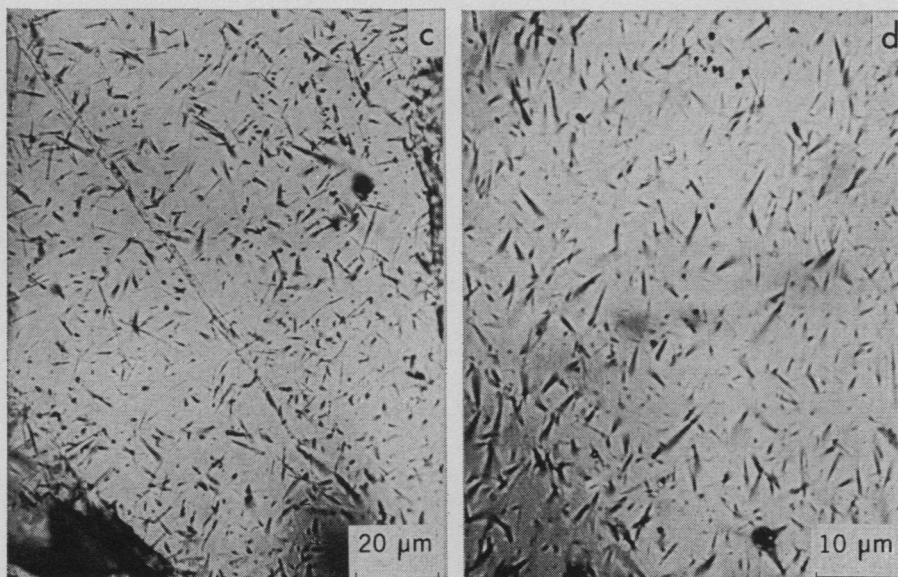


Fig. 1. Fossil cosmic-ray tracks due to iron-group nuclei in olivines: (a and b) from the Patwar meteorite; (c and d) in lunar regolith grains from the Apollo 12 mission. Part c shows sample 12028,68 (double core); part d shows sample 12041,11 (surface scoop). Tracks were revealed by etching with WN at its boiling point for 5 hours. Tracks were decorated with 0.25 unit of silver (8).