Reports

Artifacts in Polarimetry and Optical Activity in Meteorites

Abstract. *Scattered light produces spurious optical rotations of up to 80 millidegrees in commercial polarimeters. Even larger "rotations," up to 180 millidegrees, are observed when the sample simultaneously absorbs and scatters light. These effects may account for the optical activity reported in the Orgueil meteorite.*

Nagy (*1*) and Urey (*2*) have presented new data supporting earlier claims of levorotation in the Orgueil meteorite (*3*), and have attempted to rebut my negative result as well as my criticism of the earlier work (*4*). Because important questions were not covered in these papers, it seems appropriate to review the matter and to introduce additional evidence.

My criticism of Nagy's work was based on three points: (i) The solutions absorbed light strongly, and high absorbance lowers the sensitivity of the polarimeter (*5*). (ii) The solutions contained colloidal particles which scatter and depolarize light (*3*); such stray light inevitably passes through the analyzer and gives a spurious rotation on the polarimeter (*6*). (iii) When the extraction procedure is modified to remove sulfur, the meteorite extracts are nearly colorless, free of colloidal particles, and optically inactive (*4*).

Nagy has tacitly acknowledged the first point by keeping the absorbance below 0.15 in his latest experiments. This does not absolve his 1964 work, however, where cell length and amount of meteorite were greater by factors of 10 and 4, respectively.

Nagy's and Urey's rebuttals made no mention of scattering (point ii), confining their attention to absorption only. This is unfortunate, since scattering is an independent and potentially serious source of error. Rouy *et al.* (*6*) have discussed the theoretical basis of this effect, and many, including me, have confirmed it experimentally.

Apparently a further demonstration is needed. At the suggestion of Rouy and Carroll, I have performed an experiment that illustrates the effects of absorption and scattering on measurements of optical rotation. To separate the variables, I used filters and frosted-glass disks to absorb and scatter light, respectively.

The absorption spectra of the filters and frosted-glass disks (Fig. 1*a*) are compared with spectra of Nagy's Orgueil extract (*I*) and control (*II*) (Fig. 1*b; 7*). Differences in path length aside, the orange filter–frosted glass combination matches Nagy's Orgueil extract above 440 mμ, where most of his rotation data were taken.

Optical-rotation data for these samples were measured on a Rudolph automatic spectropolarimeter having a sensitivity of $\pm$ 1 millidegree (mdeg) (Fig. 2*a*). The filters alone gave only marginal levorotations of no more than 1.5 mdeg, even at wavelengths where their absorbance was greater than 2; the frosted-glass disks gave much larger rotations: up to 14 mdeg. Still larger rotations, up to 23 mdeg, were obtained with the filter–frosted glass combinations. Clearly the effects were not additive: by itself, absorption had only a slight effect, yet it enhanced the effect of scattering very significantly.

These pseudorotations were of the same magnitude as Nagy's 1964 results on Orgueil: -7 ± 5 to -23 ± 5 mdeg. Of course, quantitative comparison is difficult since Nagy did not give the original data, obtained in 1- to 20-cm cells, but quoted instead a set of values recalculated to 10-cm path length. A marginal rotation in a 1-cm cell would thus be disproportionately magnified when recalculated to 10 cm.

It is interesting that all these rotations were levo. Previously, the sign of spurious rotations caused by scattering was considered indeterminate,

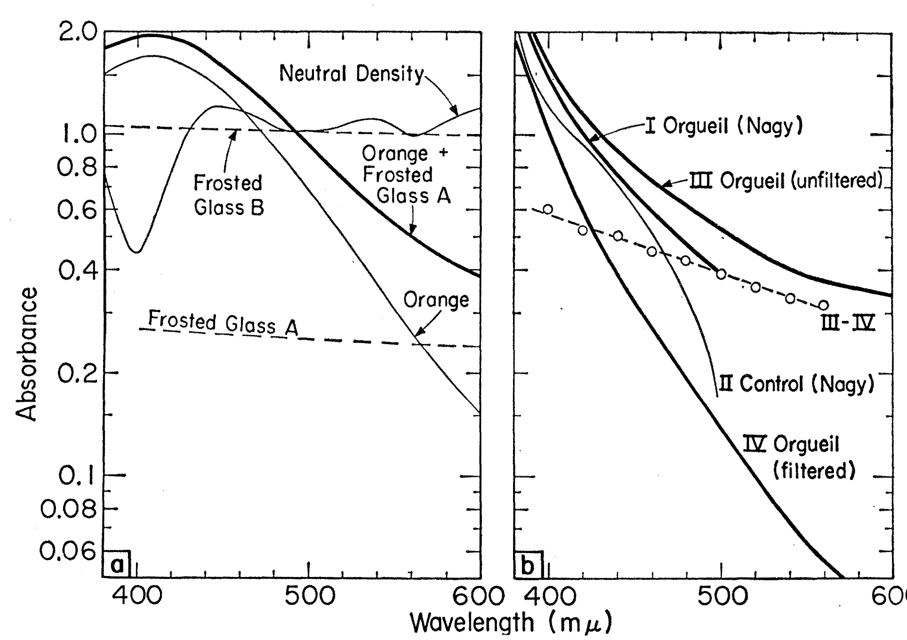

Fig. 1. Absorption spectra of filters, frosted-glass disks, and meteorite extracts. An Orgueil extract prepared by Nagy's procedure shows appreciable absorption at longer wavelengths (*III*), most of which disappears when the extract is filtered through a membrane filter (*IV*); it seems to reflect a light-scattering particulate component whose magnitude can be estimated by substraction of the two curves from one another (*III–IV*). The spectrum of Nagy's 1964 sample (*I*) can be similarly resolved into and absorbing (*IV*) and a scattering component.

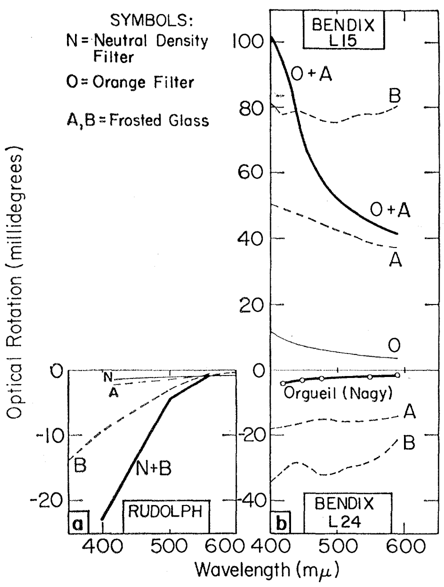

Fig. 2. Spurious optical rotations on one Rudolph automatic and two Bendix Polarmatic spectropolarimeters. Filters alone (*N, O*) give small spurious rotations, whereas frosted-glass disks give much larger ones (*A, B*). Still larger "rotations" are obtained for filter–frosted glass combinations (*N+B, O+A*). Evidently light scattering is a far more serious source of error than light absorption, especially under conditions of low light transmission. Only a small amount of light scattering would suffice to produce the "rotations" of 2 to 4 mdeg reported by Nagy for Orgueil.

but Rouy and Carroll (*8*) have shown that certain mechanical and electronic features of the polarimeter can predetermine the sign. In the specific case of the Rudolph instrument, a consistent "levo bias" exists.

Nagy's latest results (−1.7 to −4.1 mdeg) were obtained on a Bendix Polarmatic spectropolarimeter, apparently on the assumption that this instrument was free from artifacts (*1*). To verify this point, I arranged to have my filter–frosted glass combinations measured on two Bendix Polarmatic-460C spectropolarimeters, serial Nos. L15 (Purdue University) and L24 (*9*); the latter had been newly calibrated and checked. Representative data appear in Fig. 2*b*, along with Nagy's latest results on Orgueil.

Both instruments dealt rather well with absorbance alone. If care was taken to orient the filters so as to minimize birefringence, false rotations did not exceed 12 mdeg at absorbances of 2. Errors are apparently larger when the instrument is not perfectly aligned. Resnick and Yamaoka (*10*) found that the L24 gave rotations of up to 200 mdeg with optically inactive solutions of $K_2Cr_2O_7$, acridine orange, and other compounds—an effect apparently greatly reduced by realignment.

Neither instrument could handle scattering, however. The frosted-glass disks alone gave "rotations" of up to 80 mdeg; in combination with filters, up to 180 mdeg. Sign and magnitude of the effect varied from one instrument to another: the L15 instrument always gave dextrorotations, while the L24 gave levorotations one-half to one-third as large. Of the Bendix instruments mentioned by Resnik and Yamaoka, one gave dextro- and the other gave levorotations. Obviously, both the Bendix and Rudolph instruments are susceptible to scattered light. Both can yield spurious rotations considerably exceeding Nagy's meteorite rotations.

It remains to be determined whether light-scattering particles were present in Nagy's samples. Two lines of evidence suggest that they were. First, Nagy *et al.* added colloidal sulfur to some of their blanks, apparently to compensate the colloid content of their samples. Secondly, I have repeated Nagy's procedure on a 5-g sample of Orgueil meteorite. A slightly turbid solution was obtained (curve *III* in Fig. 1*b*), which, after filtration through a 0.45-μ membrane filter, became almost perfectly clear and showed decreased absorption throughout the entire spectrum (curve *IV*). Absorption due to the filterable component could be estimated by subtraction of the two curves; a typical scattering curve resulted (*III–IV*). Nagy's Orgueil curve (*1*) has a slightly steeper slope than curve *III* and thus only about two-thirds the particulate content. But it, too, can be represented by a linear combination of curve *IV* with a scattering curve. Since Nagy's extracts had been filtered through a 0.45-μ filter, the scattering material may have been colloidal.

Nagy's control, a sulfur solution to which a brown dye was added (*II*), shows drastically decreasing absorption at longer wavelengths and is evidently free of particulate matter. Obviously this control is nonrepresentative, since it tries to substitute (electronic) absorption for scattering. In their effect on polarimeters, these two phenomena are not interchangeable.

Because Nagy's procedure inevitably gives turbid or colloidal solutions, meaningful controls must contain some particulate matter. When such controls are prepared (*4*) they give a spurious rotation comparable with that observed in the meteorite (*3*). This artifact is an inevitable consequence of their absorbance and turbidity and of the shortcomings of commercial polarimeters. Apparently this point was misunderstood by Urey, who attempted to dismiss my entire work on the grounds that ". . . the people at Chicago found optical activity in inorganic substances" (*11*). Nagy's statement, "Our procedure blanks and synthetic-dye solutions containing sulfur gave no optical rotation while Hayatsu's did," reveals a similar misunderstanding.

Nagy puts much stress on the fact that in his 1964 work "The Orgueil extracts from three stones were found to be levorotatory by three independent operators on three Rudolph polarimeters in three laboratories." However, all three extracts were prepared by Nagy by a procedure that inevitably gives turbid or colloidal solutions; all three were measured immediately above the wavelength of "no transmittance." Colloids, as Rouy *et al.* (*6*) pointed out years ago, inevitably and reproducibly give false rotations, especially under conditions of marginal light transmittance. Djerassi (*5*) showed that absorption alone can give reproducible false rotations. Thus the reproducibility of the rotation is hardly an argument for its authenticity. Artifacts can be reproducible, too, and there is little doubt that a well-known artifact was present in all of Nagy's experiments.

Finally (point iii), Nagy (*1*) attributes my negative result to differences in the extraction procedure, implying that three separate 6-hour extractions with benzene, chloroform, and methanol (*4*) were not equivalent to a single 6-hour extraction with a benzene-methanol mixture (*3*). Whatever the plausibility of this suggestion, it is contradicted by Nagy's own experiments: Using my extraction procedure (but failing to remove sulfur due to insufficient cooling), Nagy obtained an apparent rotation of −84±5 mdeg at 546 mμ (*12*); he reported that "the solution was opaque" (*12*) below this wavelength. Urey (*2*) later quoted this result as −25±5 mdeg, "corrected for process blanks"; a blank correction of 59 mdeg is apparently implied.

If these results are taken at face value, my procedure is vindicated. In fact, it is proved superior, having given 12 times the rotation with one-half the amount of meteorite. This would seem to eliminate Nagy's objection.

It appears, however, that these results are not entirely above criticism. The measurement was again taken just above the absorption cutoff, although there is ample evidence that false rotations result under conditions of marginal light transmission. Compared to Nagy's 1964 extracts, the absorption cutoff was shifted 100 $m\mu$ toward the red, suggesting even greater opacity. Because sulfur was present during saponification, colloid formation must have been hard to avoid. Finally, it is not clear how much significance can be attached to a net result of 25 mdeg if the "process blank" is as large as 59 mdeg.

I wholeheartedly endorse Nagy's appeal for "slow, careful, and systematic [work], preferably in the absence of unnecessary argument." On my part, I add the plea that all work be checked by meaningful controls, and that the plentiful evidence of artifacts in polarimetry be given due attention instead of being disregarded.

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References and Notes

1. B. Nagy, *Science* **150**, 1846 (1965).
2. H. C. Urey, *ibid.* **151**, 157 (1966).
3. B. Nagy *et al.*, *Nature* **202**, 228 (1964).
4. R. Hayatsu, *Science* **149**, 443 (1965).
5. A. L. Rouy and B. Carroll, *Anal. Chem.* **33**, 594 (1961); C. Djerassi, E. Lund, E. Bunnerberg, J. C. Sheehan, *J. Org. Chem.* **26**, 4509 (1961).
6. A. L. Rouy, B. Carroll, T. J. Quigley, *ibid.* **35**, 627 (1963); see Eq. 1 and subsequent discussion.
7. Nagy *et al.* (*3*) indicated neither cell length nor absorbance scale in their fig. 2; nor did they respond to my request for further information. I therefore read off relative absorbances with a ruler and plotted them on semilogarithmic paper. This procedure faithfully reproduces the shape of the spectrum but leaves its vertical position undetermined. Since curves *I* and *III* (Fig. 1*b*) both consist of an absorbing and a scattering component (see below), curve *I* was placed at the position where curve *IV* correctly represents its absorbing component. The scattering component can then be found by simple subtraction of *IV* from *I*.
8. A. L. Rouy and B. Carroll, *Anal. Chem.*, in press; "On the reported optical activity for the Orgueil meteorite," in preparation.
9. The filters were measured in cylindrical holders, 39 by 22 mm outside diameter, with an aperture of 6 mm. The frosted-glass disks were inserted at the end facing the light source; the filters, at the opposite end. I thank M. E. Lipschutz, Purdue University. for these measurements.
10. R. A. Resnik and K. Yamaoka, "An instrumental artifact in spectropolarimetry," *Biopolymers*, in press.
11. H. C. Urey, "Organic matter in meteorites: a review," paper presented before Nat. Acad. Sci. U.S., Autumn Meeting, Seattle, Wash., 12 Oct. 1965.
12. B. Nagy, letter to E. Anders, 24 Feb. 1965; these results were also quoted in (*4*).
13. Work aided by NASA grant NsG-366. I thank Edward Anders, Benjamin Carroll, and Auguste L. Rouy for advice; and L. Katzin and E. Gulyas, Argonne National Laboratory, for use of their Rudolph spectropolarimeter.

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Antarctic Pack Ice: Boundaries Established from Nimbus I Pictures

Abstract. *Television and photofacsimile-constructed infrared pictures taken by the Nimbus I meteorological satellite between 28 August and 22 September 1964 were analyzed for indications of the pack-ice boundary around Antarctica. Mean ice boundaries were established around the entire continent from both TV and infrared pictures, from which were estimated pack-ice areas of 19.81 by 10^6 and 16.78 by 10^6 square kilometers, respectively; the difference is attributed to difference in subjective discernment of a boundary.*

Advanced Vidicon camera system (AVCS) television pictures and high-resolution infrared-radiometer (HRIR) photofacsimile pictures taken by Nimbus I, the first polar-orbiting, altitude-controlled, meteorological satellite, of the Antarctic continent and seas between 28 August and 22 September 1964 were analyzed for indications of the pack-ice boundary and for cloud systems. The pictures of sea ice were remarkably clear, particularly of such areas as the Weddell Sea. Both Figs. 1 and 2 (*1*) show the ice texture and the continental boundary; Fig. 2 shows also the pack-ice boundary and various cloud systems. Not all areas were as well covered; cloud systems frequently made determination of the sea-ice boundary difficult, particularly where over- or underexposure permitted little distinction between ice and cloud. But such difficulties were minor in view of the outstanding fidelity of the pictures, which were taken from altitudes between 640 and 933 km (apogee).

Boundaries for the ice edge were decided for the various longitudinal sectors from the overlapping orbital picture passes. For some sectors of which many picture sequences were available, variations in the ice boundary could be studied; other sectors barely appeared in the fringes of pictures, and still others were not pictured at all (they were spanned by simple interpolation). Grid lines of latitude and longitude were generated by computer at the time of read-out for some of the pictures. This, however, did not aid in proper location of the ice boundary in all instances: in many picture composites having a well defined grid

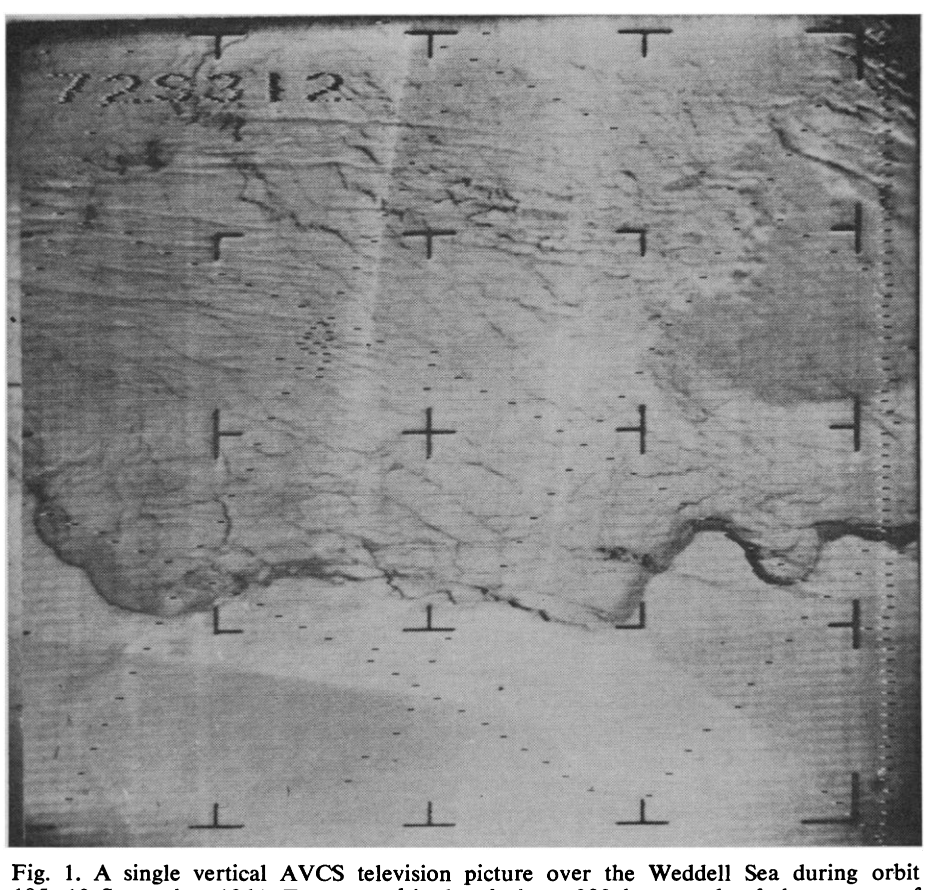

Fig. 1. A single vertical AVCS television picture over the Weddell Sea during orbit 195, 10 September 1964. From an altitude of about 900 km, much of the texture of the sea ice is apparent.