COMMUNICATIONS TO THE EDITOR

THE "STAR TRAIL" METHOD FOR THE SPECTROGRAPHIC QUANTITATIVE DETERMINATION OF THE ELEMENTS

Sir:

Diligent search of the voluminous literature has failed to disclose the "Star Trail" method for the spectrographic quantitative determination of the elements as described below. A bright line is isolated from a spectrum by interposing a slotted light stop between the refracting element and the telescope of a spectroscope. The image of the line so isolated falls upon a film affixed to a rapidly rotating drum which spreads out this line into a band. The rotation serves to equalize any flickering due to any cause and to render the band of uniform density, which depends upon the concentration of the given element in the solution employed and upon the time during which the film is exposed to the light. The drum carrying the film can be racked up or down so as to expose different parts of the film, as desired.

Spectra due to different concentrations of the same element, employed as standards, are exposed in a series with the unknown concentration on the same film as a succession of bands, keeping time of exposure and speed of rotation of the film as constants. The bands of different density can be compared directly by cutting the film across all the bands and bringing the latter into direct alignment. Density can also be controlled by the manner of developing the film.

Experiments with sodium chloride in concentrations varying between 0.500 and 0.0250% and exposure of five minutes to a portrait panchromatic film gave satisfactory indications of the value of the method.

Work is now proceeding at the University of Illinois with special reference to the application of the method to the quantitative analysis of the alkali metals.

Department of Chemistry
University of Illinois
Urbana, Illinois

A. C. Shead
G. Frederick Smith

Received October 10, 1930
Published December 18, 1930

THE PARACHORS OF TWO ISOMERIC CHLORODINITROBENZENES

Sir:

In a recent communication[1] Sickman and Menzies reported the results of a determination of the parachor of 1-chloro-3,4-dinitrobenzene from surface tension measurements at 40 to 60°. This was found to be approximately the same, allowing for "drift of parachor with temperature," as that evaluated from Jaeger's measurements[2] of the surface tension of the

---

[1] Sickman and Menzies, This Journal, **52**, 3327 (1930).

[2] Jaeger, *Z. anorg. allgem. Chem.*, **101**, 117 (1917).

1-chloro-2,4-dinitro isomer at 60 to 95°. After pointing out that in both these cases the observed parachor is more than 3% lower than that calculated from Sugden's atomic and structural constants,[3] the authors added, "the latter have been recalculated by Mumford and Phillips.[4] By using these newer constants, the discrepancy is not diminished...." As will be apparent from the following table, however, this statement is incorrect, for the use of the reëvaluated constants materially reduces the difference between calculated and observed values.

TABLE I

PARACHORS OF THE CHLORODINITROBENZENES

Compound	Parachor
1-Chloro-3,4-dinitrobenzene (Sickman and Menzies 40 to 60°)	347.4
1-Chloro-2,4-dinitrobenzene (Jaeger 60 to 95°)	348.2
Calculated for either compound (Sugden)	358.3
Calculated for either compound (Mumford and Phillips)	353.2

The latter value, which was, incidentally, quoted in our original paper on the reëvaluation[5] is the algebraic sum of the constants for the constituent atoms (*viz.*, 6 of carbon, 3 of hydrogen, 1 of chlorine, 2 of nitrogen and 4 of oxygen), and those for the various structural features (*viz.*, 1 six-membered ring, 5 non-polar and 2 semi-polar double bonds) *together with the appropriate strain constants*, in this case one of -3 units associated with each of the nitro groups, and a complex one of $-(3.4 + 2.4 + 2.2) = -8$ units due to the unsymmetrical accumulation of three negative groups around the benzene nucleus.

It must be noted further that in the case of Jaeger's data for 1-chloro-2,4-dinitrobenzene, only three measurements at lower temperatures have been utilized by Sickman and Menzies. A considerably higher mean parachor is obtained if the other six determinations are also taken into account, as has been done in Table II.

TABLE II

JAEGER'S DATA FOR 1-CHLORO-2,4-DINITROBENZENE

Temp., °C.	Surface tension, dynes/cm.	Density	Parachor
60.4	45.5	1.515	347.2
76.2	43.9	1.497	348.2
95	42.2	1.477	349.4
114	40.4	1.455	350.9
136	38.3	1.432	351.8
155.1	36.4	1.412	352.3
175.5	34.5	1.391	352.8
190	32.9	1.378	351.9
204.2	31.5	1.365	351.5

---

[3] Sugden, *J. Chem. Soc.*, **125**, 1177 (1924).

[4] Mumford and Phillips, *ibid.*, 2112 (1929).

[5] Mumford and Phillips, Ref. 4, Table V, p. 2118.

The average of all the measurements is 350.7, but as the parachor rapidly attains and maintains a mean value of about 351.6, it is evident that *this* should be taken as representative of the compound in question, and the values in the vicinity of the melting point regarded as anomalous. This value, which was quoted in our original paper as the observed parachor of 1-chloro-2,4-dinitrobenzene, is less than 0.5% lower than that calculated from our reëvaluated constants, namely, 353.2, and it would, therefore, seem unnecessary to look further for the cause of the apparent discrepancy.

In the case of the 1-chloro-3,4-dinitro isomer the observed parachors likewise increase rapidly with temperature in the vicinity of the melting point and it seems likely that here also a higher and truer mean value would have been obtained had the measurements been extended to higher temperatures.

EAST GRIMSTEAD
SALISBURY
WILTS, ENGLAND
S. A. MUMFORD
J. W. C. PHILLIPS

RECEIVED NOVEMBER 6, 1930
PUBLISHED DECEMBER 18, 1930

PARACHORS OF ISOMERIC CHLORODINITROBENZENES

Sir:

Through the courtesy of the Editor, we are enabled to add in this issue a few words on the subject of the foregoing interesting note.

In Table V of their cited article, Mumford and Phillips tabulate 361.2 under the caption "Σ At. P." and −8 under the caption σ (or strain constants). Since the strain constants for the nitro group are not referred to until two pages later, we had not understood that these were included in the value 361.2, which we took to be a misprint for 367.2, the value for the sum of atomic and structural constants. The interpretation of the authors is, therefore, very welcome.

The reason we made our measurements in the temperature range 40–60° was because this was the range used by Müller, whose enormous discrepancy it was our primary purpose to examine.

In comparing the results of Jaeger for the other isomer, we thought it fairest to use the portion of his temperature range closest to 40–60°; and, because we noticed that there was an apparent drift of this parachor with temperature, we corrected the value for drift in order to make the best possible comparison. When a parachor exhibits such drift, the best criterion for its absolute value is, of course, debatable.

DEPARTMENT OF CHEMISTRY
PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY
D. V. SICKMAN
ALAN W. C. MENZIES

RECEIVED NOVEMBER 14, 1930
PUBLISHED DECEMBER 18, 1930