

250 and 315°. A comparison of the reaction rates in packed and unpacked vessels shows not only that the reaction is homogeneous but that it is of the chain type.

The change in composition of the condensable reaction products with time of contact shows that the oxidation proceeds through the stages glyoxal-formaldehyde-formic acid. The gaseous products consist mainly of carbon monoxide, together with carbon dioxide and hydrogen. A study of the change in gas composition with contact time indicates that carbon monoxide originates mainly from the direct decomposition of glyoxal, and that carbon dioxide is due to oxidation or decomposition of formic acid, whereas the origin of the traces of hydrogen is at present uncertain.

The velocity of reaction is proportional to the square of the acetylene concentration and is independent of the oxygen concentration.

In packed vessels the homogeneous oxidation is almost entirely suppressed, and a heterogeneous oxidation of acetylene on the glass surface directly to carbon dioxide and water takes place. The rate is roughly proportional to the first power of the acetylene and oxygen concentrations. The mechanism of the reaction has been discussed.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE PHYSICS DEPARTMENT, ALABAMA POLYTECHNIC INSTITUTE]

A MAGNETO-OPTIC METHOD OF CHEMICAL ANALYSIS

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This paper reports some results of a method which promises to be of value as a new means of chemical analysis. It also suggests a new angle of approach to certain aspects of the problem of ionization in liquids. The method is a refinement of one previously described by Allison¹ in the investigations of the time lag differences of the Faraday effect behind the magnetic field in certain liquids as a function of the wave length of the light used.

In a study of solutions it was subsequently found that each chemical compound, regardless of the presence of other substances, produces its characteristic minimum (or minima) of light intensity, which persists until the concentration is reduced to about 1 part in 10¹¹.² This fact suggested that the method might have application in some cases of chemical analysis.

The authors³ have extended these findings of Allison to include a rather comprehensive series of solutions of chlorides, nitrates, sulfates and hydroxides.

¹ Allison, *Phys. Rev.*, **30**, 66 (1927).

² Allison, *ibid.*, **31**, 313 (1928).

³ Allison and Murphy, *ibid.*, **35**, 124 (1930).

The experimental arrangement is diagrammatically shown in Fig. 1. The apparatus together with its manipulation has already been described.^{1,2,3} A kenetron tube *K* replaces the Wehnelt interrupter of the original set-up, the condenser *C* being charged from the high voltage side of the transformer *M*. Sliding rheostats *R*₁ and *R*₂ are in series with the primaries of the main transformer and the filament transformer, respectively. *B*₁ and *B*₂ represent the cylindrical cells which are placed co-axially within the helices of wire, *N*₁ and *N*₂ the polarizing and analyzing Nicol prisms, *L* a converging lens, *F* Wratten filters and *T*₁*T*₁ and *T*₂*T*₂ the sliding trolleys. A steady source of light in connection with a monochromator has at times been used instead of the spark *A*, the latter being screened.

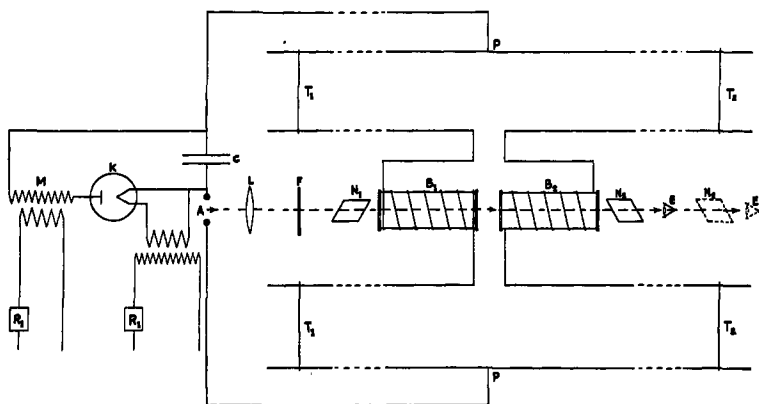


Fig. 1.—Diagram of apparatus and connections.

For some time we have often found convenient a combination of the air or light path and the wire path in measuring these time effects. The sliding trolley, although itself equipped with a vernier, becomes the coarser scale, while the finer settings are made by displacing the cell *B*₂ by means of a rack and pinion motion. The trolley is first set at a point within a few centimeters of the position at which a minimum is observed and the minimum is then finally located with surprising precision on the rack and pinion scale. The wire and light paths are then simply combined.

Representative results are given in Table I. The compounds of each series are arranged in columns in the order of the increasing chemical equivalents of their metallic elements. In the first column under each compound are recorded the positions of the characteristic minima of the compound as read on the wire path scale. In the second columns are tabulated the differential time lags, all of which are with reference to carbon bisulfide. The zero of the wire path scale is at 15.00. The differential lags are therefore found by subtracting the scale readings of the minima from this zero point, since the scale is laid off in units of 30 cm. The lags are thus

TABLE I
SCALE READINGS OF CHARACTERISTIC MINIMA AND DIFFERENTIAL TIME LAGS WITH
REFERENCE TO CARBON BISULFIDE

Scale reading	Seconds $\times 10^{-3}$	Scale reading	Seconds $\times 10^{-3}$	Scale reading	Seconds $\times 10^{-3}$	Scale reading	Seconds $\times 10^{-3}$
HCl		HNO ₃		H ₂ SO ₄		HOH	
15.85	-0.85	5.50	9.50	8.43	6.57	9.30	5.70
15.95	-.95	5.61	9.39	8.65	6.35		
LiCl		LiNO ₃		Li ₂ SO ₄		LiOH	
16.22	-1.22	5.85	9.15	9.00	6.00	10.03	4.97
16.45	-1.45	5.95	9.05	9.10	5.90	10.18	4.82
AlCl ₃		Al(NO ₃) ₃		Al ₂ (SO ₄) ₃		Al(OH) ₃	
16.58	-1.58	6.10	8.90	9.66	5.34	10.37	4.63
MgCl ₂		Mg(NO ₃) ₂		MgSO ₄		Mg(OH) ₂	
16.82	-1.82	6.20	8.80	10.04	4.96		
16.90	-1.90	6.25	8.75	10.40	4.60		
17.03	-2.03	6.30	8.70	10.62	4.38		
NH ₄ Cl		NH ₄ NO ₃		(NH ₄) ₂ SO ₄		NH ₄ OH	
17.82	-2.82	6.80	8.20	11.21	3.79	11.05	3.95
FeCl ₃		Fe(NO ₃) ₃		Fe ₂ (SO ₄) ₃		Fe(OH) ₃	
17.96	-2.96	6.83	8.17	11.32	3.68	11.60	3.40
18.05	-3.05	6.90	8.10	11.45	3.55	11.74	3.26
CaCl ₂		Ca(NO ₃) ₂		CaSO ₄		Ca(OH) ₂	
18.44	-3.44	7.17	7.83	11.54	3.46	12.37	2.63
18.66	-3.66	7.20	7.80	12.05	2.95	12.57	2.43
NaCl		NaNO ₃		Na ₂ SO ₄		NaOH	
18.73	-3.73	7.21	7.79	13.00	2.00	13.47	1.53
AsCl ₃		As(NO ₃) ₃		As ₂ (SO ₄) ₃		As(OH) ₃	
18.98	-3.98			13.17	1.83		
CrCl ₂		Cr(NO ₃) ₂		CrSO ₄		Cr(OH) ₂	
19.15	-4.15	6.50	8.50				
MnCl ₂		Mn(NO ₃) ₂		MnSO ₄		Mn(OH) ₂	
19.22	-4.22	7.29	7.71	13.67	1.33	13.95	1.05
FeCl ₂		Fe(NO ₃) ₂		FeSO ₄		Fe(OH) ₂	
19.25	-4.25			13.90	1.10		
19.40	-4.40			14.20	0.80		
CoCl ₂		Co(NO ₃) ₂		CoSO ₄		Co(OH) ₂	
20.15	-5.15	7.30	7.70	14.40	0.60	14.74	0.26
NiCl ₂		Ni(NO ₃) ₂		NiSO ₄		Ni(OH) ₂	
20.30	-5.30	7.31	7.69	14.52	0.48	15.28	-0.28
20.40	-5.40	7.34	7.66	14.66	.34	15.60	-.60

TABLE I (Continued)

Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$
CuCl₂		Cu(NO₃)₂		CuSO₄		Cu(OH)₂	
20.48	-5.48	7.40	7.60	14.80	0.20	16.04	-1.04
20.68	-5.68	7.43	7.57	15.00	.00	16.35	-1.35
ZnCl₂		Zn(NO₃)₂		ZnSO₄		Zn(OH)₂	
21.08	-6.08	7.54	7.46	15.21	-0.21	16.27	-1.27
21.40	-6.40	7.56	7.44	15.42	-.42	16.52	-1.52
21.73	-6.73	7.67	7.33	15.75	-.75	16.93	-1.93
21.85	-6.85	7.70	7.30	16.03	-1.03	17.20	-2.20
KCl		KNO₃		K₂SO₄		KOH	
22.50	-7.50	7.82	7.18	16.74	-1.74	19.54	-4.54
22.87	-7.87	7.84	7.16	16.98	-1.98	19.95	-4.95
SbCl₃		Sb(NO₃)₃		Sb₂(SO₄)₃		Sb(OH)₃	
23.30	-8.30			17.96	-2.96	19.65	-4.65
23.66	-8.66			18.13	-3.13	19.90	-4.90
SrCl₂		Sr(NO₃)₂		SrSO₄		Sr(OH)₂	
24.35	-9.35	8.00	7.00			20.33	-5.33
24.59	-9.59	8.30	6.70			20.92	-5.92
CdCl₂		Cd(NO₃)₂		CdSO₄		Cd(OH)₂	
25.06	-10.06			18.50	-3.50		
25.28	-10.28			18.68	-3.68		
25.54	-10.54			18.81	-3.81		
25.90	-10.90			19.00	-4.00		
26.10	-11.10			19.17	-4.17		
26.25	-11.25			19.48	-4.48		
SnCl₂		Sn(NO₃)₂		SnSO₄		Sn(OH)₂	
27.40	-12.40	8.70	6.30	20.10	-5.10		
27.58	-12.58	8.74	6.26	20.40	-5.40		
27.88	-12.88	8.80	6.20	20.62	-5.62		
28.25	-13.25	8.83	6.17	21.00	-6.00		
28.54	-13.54	8.88	6.12	21.27	-6.27		
28.82	-13.82	8.90	6.10	21.40	-6.40		
29.23	-14.23	8.95	6.05	21.80	-6.80		
29.55	-14.55	9.00	6.00	22.06	-7.06		
29.80	-14.80	9.12	5.88	22.54	-7.54		
30.10	-15.10	9.21	5.79	22.81	-7.81		
30.30	-15.30	9.28	5.72	23.22	-8.22		
CuCl		CuNO₃		Cu₂SO₄		CuOH	
30.38	-15.38	9.35	5.65				
30.68	-15.68	9.50	5.50				
BaCl₂		Ba(NO₃)₂		BaSO₄		Ba(OH)₂	
30.80	-15.80	9.45	5.55	23.55	-8.55		
31.18	-16.18	9.50	5.50	23.78	-8.78		
31.35	-16.35	9.58	5.42	23.98	-8.98		
31.65	-16.65	9.72	5.28	24.20	-9.20		

TABLE I (Concluded)

Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$	Scale reading	Seconds $\times 10^{-9}$
PbCl ₂		Pb(NO ₃) ₂		PbSO ₄		Pb(OH) ₂	
36.90	-21.90	9.95	5.05	23.82	-8.82	19.18	-4.18
37.07	-22.07	10.08	4.92	24.36	-9.36	19.44	-4.44
37.30	-22.30	10.30	4.70	24.72	-9.72	19.65	-4.65
37.68	-22.68	10.46	4.54	25.10	-10.10	19.86	-4.86
AgCl		AgNO ₃		Ag ₂ SO ₄		AgOH	
38.65	-23.65	10.60	4.40	26.17	-11.17		
39.18	-24.18	10.80	4.20	26.82	-11.82		
HgCl		HgNO ₃		Hg ₂ SO ₄		HgOH	
40.10	-25.10	10.82	4.18	27.75	-12.75	19.40	-4.40
40.42	-25.42	10.93	4.07	28.04	-13.04	19.60	-4.60
40.86	-25.86	11.01	3.99	28.30	-13.30	19.74	-4.74
41.12	-26.12	11.16	3.84	28.66	-13.66	20.00	-5.00
41.34	-26.34	11.28	3.72	29.06	-14.06	20.37	-5.37
41.65	-26.65	11.42	3.58	29.48	-14.48	20.70	-5.70
42.10	-27.10	11.52	3.48	29.88	-14.88	20.96	-5.96
TiCl		TiNO ₃		Ti ₂ SO ₄		TiOH	
42.65	-27.65	11.15	3.85	30.20	-15.20	21.40	-6.40
42.95	-27.95	11.40	3.60	30.30	-15.30	21.70	-6.70

computed on the assumption that the electric surges in the wires travel with the speed of light, because in practice it is more convenient with a given set-up to adhere strictly to the readings on the wire path scale and because we no longer find it worth while to check the readings on the light path scale. There has not been opportunity, for lack of both time and material, to locate the minima corresponding to those compounds for which no values appear in the table. Some salts, such as cuprous nitrate and stannous nitrate, were obtained by the addition of the corresponding acid to dilute solutions of the chlorides. We are publishing data for only such hydroxides as we have been able to procure, though we do find in general the hydroxides present when the salts of the metals are in solution.

Since the position of each minimum corresponding to a compound is tabulated in terms of a scale whose units are marked off in lengths of 30 cm., which in time units have the value of 10^{-9} sec., the second decimal refers to a length of 3 mm. or a time of 10^{-11} sec. The various regions of the scale occupied by the nitrates, hydroxides, sulfates and chlorides will be noted from the data of the table. The chlorides have the advantage of what may be termed greater resolving power in the location of minima. In seeking to determine the presence of a metal, a very valuable check is afforded by observing the minima corresponding to each of the four compounds. There are overlapping regions, as will be seen from a study of the table, but when one gains familiarity with the order in which the minima occur,

there is little ground for confusion. It should be kept in mind that these time intervals recorded are differential, the time lag for each compound being with reference to carbon bisulfide. (Other liquids than carbon bisulfide have been used in cell B_1 . When this is done the characteristic minima due to compounds in B_2 fall at different parts of the scale in consistent agreement with the differential time lag between the new liquid in B_1 and carbon bisulfide.)

After reading the minima of a number of compounds, it appeared upon a study of the results that the positions of the minima were functions of the atomic weights of the metallic elements of the compounds or, more precisely, of the atomic weights divided by the valence, that is, the chemical equivalents. In other words, the differential time lag in general decreases with increasing chemical equivalent. In each of the four series of compounds of Table I the longest differential lag is thus produced by the compounds of hydrogen, the shortest by those of thallium. Furthermore, elements which have two different valences exhibit as a rule two minima, or two series of minima, in different regions of the scale corresponding to the chemical equivalents in the two cases, the number of minima being the same for each valence. Cases of more than two valences have not been studied. There are several slight exceptions to the law of decrease of differential lags with chemical equivalence. Among these will be noted the minima of the compounds of nickel and cobalt and those of some of the heavy metals which have a number of isotopes, the minima of the latter compounds overlapping in certain regions of the scale. In reading across the table, it will be seen that for any metallic element there also exists this relationship between differential time lag and chemical equivalent in the case of the chlorides, sulfates and nitrates, the hydroxides falling somewhat out of line in this respect.

It will be further noted from the tabulated results that each compound produces either a single minimum or two or more close minima. The number of these minima, with few exceptions, is the same as the number of the known isotopes of the metallic elements of the compounds, whether the elements be in the chloride, nitrate, sulfate or hydroxide form. This is in keeping with the relationship discussed in the preceding paragraph, namely, the variation of the differential lag with atomic mass. The isotopes of the metallic element, in each series of compounds, alone seem to be operative in producing minima. Hydrochloric, nitric and sulfuric acids each produce two minima, for which we are unable to account. It will now be seen that the cobalt minimum takes its place regularly with respect to the minimum of the heavier isotope of nickel but not with respect to that of the lighter.

Several compounds at great dilution behave as if the magnetic rotation exerted by them is of negative sign. For example, repeated observations

failed to reveal minima characteristic of ferric sulfate. Upon reversing the field in B_2 , however, the two minima appeared in the appropriate region of the scale, as shown in the table. These results are suggestive of those reported by Roberts⁴ and others concerning the magnetic rotary dispersion of certain paramagnetic solutions. It is planned to make further study of this behavior of solutions.

Since water in all the reported results was the solvent of the compounds, considerable time has been devoted to searching for minima when the purest water which we have available fills the cell B_2 , namely, that distilled in quartz. There are some four or five minima distributed over the scale which we have been unable to remove by redistillations. One of these, because of its distinctness, we have attributed to water. The others we have been unable to identify. Some are doubtless due to compounds dissolved from the glass cell even during the short time the water is in contact with the glass before an observation can be made. These unknown minima, being always at fixed points of the scale, are not a source of confusion but they are actually an advantage in supplying fiducial points along the scale. It is planned to investigate further the causes of these minima.

We have thus far had the opportunity to make a study of practically no inorganic compounds except those listed in the table. A great deal of laborious observation is required to locate the characteristic minima with precision for a large series of compounds. Once the table is determined, however, it affords a rather rapid means of analysis for any compounds of the series. It is planned to construct in the near future tables for carbonates, phosphates, etc., as well as for certain organic compounds. There is reason to believe that this method is applicable to most, if not all, compounds.

The method appears to be a reliable one, as attested by a large number of successful tests and chemical analyses. Several advantages inherent in it may be suggested. One is the speed with which the presence of a compound may be detected. Another is due to the fact that the sample is not destroyed by the analysis, since it is merely subjected to the passage of a beam of light through it. Inasmuch as very small quantities are easily detectable, substances which are very slightly soluble, whether transparent or opaque, readily lend themselves to this sort of analysis. It may be further remarked that the apparatus necessary is comparatively inexpensive. Its operation, however, requires the attainment of a considerable amount of experience and technique on the part of the observer. It is not to be expected, in the present stage of development, that the method will yield dependable results in the hands of the average observer. Improvements are still being made, however, and it is hoped that ultimately it will be adapted to more general usage.

⁴ R. W. Roberts, *Phil. Mag.*, 9, 361 (1930).

An analogy with spectrum analysis may be of interest. Instead of spectrum lines characteristic of the chemical elements, we have disposed along a scale (some 25 feet long) the minima characteristic not of the elements alone but of the chemical compounds. For example, the various compounds of sodium, NaCl, NaNO₃, Na₂SO₄, NaOH, show minima in different regions of the scale, by means of which each compound when in solution may be recognized. The metallic element in the compound seems to be chiefly effective in producing minima. At any rate, we have found no minima which we could ascribe to the negative part of the molecule. Such minima, of course, may occur in the extended regions of the scale which have not been carefully explored.

Since we find it far more convenient to use the wire path method (or a combination of the wire and light paths), observations have been carried out on the three different set-ups, all built of somewhat different dimensions and in two different rooms, to determine how the positions of the minima correspond on different scales as read on the wire path scale. It is found that, when the set-ups are constructed symmetrically, there is very close agreement in the differences between corresponding minima on the three. Each new set-up, however, should have its wire path calibrated by finding the exact positions of the characteristic minima corresponding to the compounds for which analyses are subsequently to be made. The positions of the minima are not changed, within the errors of observations, by wide variations in the resistance, capacitance or inductance of the circuit, though the distinctness of the minima is affected by such changes. Optimum conditions for sharp minima may be found by experiment through the adjustments of the constants of the circuits. The beginner is likely to meet with considerable difficulty here, since he will probably fail to note the minima at all until this optimum condition is approximated. No fixed rules can be laid down for this adjustment, owing to the variations in the constants of different circuits. It is especially important that the capacity of the condenser be adjustable to the proper magnitude.

Settings on a minimum may be repeated by the same observer, or by different observers, within a deviation of a very few millimeters. Rather close minima may therefore be distinguished with considerable ease. The minima are surprisingly sharp, some more so than others. The hydroxides produce minima which are least sharp and most difficult to locate with precision.

The sensitiveness of the method has proved to be surprisingly great. Tests have been carried out on a representative number of solutions of compounds of graded concentrations. The results show that about 1 part in 10¹¹ of the solvent can be detected. This is true for both organic and inorganic compounds. The minima show no appreciable change in distinctness at various stages of concentration until the dilution at which they

vanish is approached, when they gradually fade out, usually between 1 part in 10^{11} and 1 part in 10^{12} . The sensitivity is not appreciably affected by the presence of other compounds in the solution, but it depends somewhat upon the observer, the chemical compound and the adjustment of the apparatus. The sensitiveness of this magneto-optic method in comparison with other methods is indicated in the following table (the data are quoted from Aston).⁵

	Mass in gm. at which the method breaks down
Ordinary chemical balance	8.5×10^{-5}
Quartz micro-balance	2.58×10^{-9}
Spectrum analysis (Na lines)	3.22×10^{-10}
Ordinary microscope	6.25×10^{-13}
Ultramicroscope	2.38×10^{-18}
	5.15×10^{-22}
Magneto-optic method about	1×10^{-11}

It is recognized, of course, that the results reported in this paper cannot be accounted for on the classical theory of magneto-optics nor are they in accord with experiments on the variation of the magnetic rotation with concentration. Furthermore, our findings are difficult perhaps to reconcile with the modern theory concerning ionization in very dilute solutions. While we are as yet unable to offer a satisfactory interpretation of our results, there are several points that should be mentioned. The effect is certainly a time effect, because the characteristic minima are produced by changes in the light path alone, as well as by changes in the wire path. This is further borne out by the fact that when the two cells are exchanged, the positions of the minima are shifted to points of the scale in keeping with this interpretation. Furthermore, when a tube of water is introduced between B_1 and B_2 , the position of a given minimum is displaced forward on the light path scale in proportion to the lengthening of the optical path by the water. (This is of additional interest in suggesting a new method for the direct measurement of the speed of light in transparent liquids.) In searching for oscillations several methods were employed. A test coil attached to a vacuum thermocouple was placed alternately in the helix of B_1 and B_2 and the trolleys moved along the scale. The deflecting instrument showed no indication of maxima or minima. A neon tube also failed to give such indications when moved along the scale between the trolley wires. A thermo-galvanometer connected in series with one branch of the circuit showed no maximum and minimum readings corresponding to different points of the scale as the trolley was displaced. An effort was also made to detect oscillations by resonance in a vacuum tube circuit set up for the purpose, but no oscillations capable of affecting our results could be found.

⁵ Aston, *J. Franklin Inst.*, 193, 583 (1922).

In the present light of our investigations we believe that the phenomena are most probably to be interpreted as due to differential time lags in the Faraday effect. Such an abnormal magnetic rotation in these very weak solutions may possibly be accounted for because of several factors, namely, the high frequency of the magnetic field, the enormous instantaneous amperage and the steepness of the wave front of the transient surges of current. That the form of wave front may be effective is suggested from our experience last summer, with the coming of the first rains. As our research room, situated in the basement, became more and more humid, the minima entirely disappeared, though no changes in our apparatus had been made. Corona losses were obviously rather large. We tried the expedient of bringing in several heaters, when, within a few hours, the minima were visible again. We found it necessary to control the humidity in this way throughout the summer. During nine months of the year no such control is necessary. While as pointed out above a differential Faraday time lag still seems the most plausible interpretation, the experimental results herein reported would not be undermined should this interpretation subsequently be found untenable, since these results are based upon actual measures of some time effect.

Investigations are now in progress to ascertain to what extent the method is applicable for the quantitative estimation of compounds present in extremely small amounts. The preliminary results are very encouraging. With a series of increasing and known concentrations of a given compound in water (serving as standards), observations are carried out to find at what concentration the characteristic minima of the compound first appear. Most compounds for which quantitative tests have been made reveal their presence when the concentration is near 1 part in 10^{11} . By making observations on a corresponding series of increasing concentrations of the unknown solution in water, one notes as before the concentration of the unknown solution in which the minima characteristic of the particular compound are first observed. By a simple computation the quantity of the compound in the unknown solution may then be determined. As the gradations in the increasing concentrations of the solution may be made as small as one desires, it is believed that the method has possibilities of an accuracy in quantitative analysis that will render it valuable for some purposes. In a later paper it is planned to give a more definite report on the quantitative aspects of the method.

Our recently reported evidence⁶ of the presence of element 87 in certain samples of pollucite and lepidolite ores is based upon the location of minima characteristic of an element of the atomic weight and valence ascribed to eka-caesium. An additional report of this investigation is contemplated in the near future.

⁶ Allison and Murphy, *Phys. Rev.*, **35**, 285 (1930).

It is a pleasure to acknowledge the helpful coöperation of a number of chemists. We mention in particular our indebtedness to Dr. J. L. McGhee, of Emory University, who has contributed greatly by his collaboration in the work of chemical analysis and otherwise; to Professor H. D. Jones, formerly our colleague and at the present time an industrial chemist, who has checked some of our observations and has made analyses by the method; to our colleague, Professor H. M. Martin, whose advice in problems of inorganic chemistry has been frequently sought; in fact, to the entire faculty of chemistry in this Institution for their cordial attitude of coöperation. We wish also to express our thanks to Mr. J. H. Christensen, student assistant in physics, for taking many observations, particularly with the hydroxides, and for making a number of checks on our work.

Summary

1. Each compound studied produces its own characteristic minimum, or minima, of light, regardless of the presence of other compounds.
2. The characteristic minima of those compounds for which quantitative tests have been made do not disappear until the concentration is reduced to about one part of the compound in 10^{11} parts of water.
3. These minima appear at points along the scale in the order of the chemical equivalents of the metallic elements of the compounds, or the differential time lag is some inverse function of the chemical equivalent.
4. The number of characteristic minima, with few exceptions, is equal to the number of known isotopes of the metallic element of the compound.
5. The method promises to be of value in quantitative as well as in qualitative analysis in work dealing with very small quantities of materials.

AUBURN, ALABAMA

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HEATS OF NEUTRALIZATION BY THE CONTINUOUS FLOW CALORIMETER

BY LOUIS J. GILLESPIE, RAYMOND H. LAMBERT AND JOHN A. GIBSON, JR.

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The continuous flow calorimeter¹ served to locate a serious error in an accepted value² for the heat of neutralization of sodium hydroxide with hydrochloric acid, in agreement with the findings of Richards and Rowe,³ which were published at the same time. Richards and his collaborators at Harvard have given a large body of data which seem to be of high precision, and repetition or extension of their measurements appears pointless

¹ Keyes, Gillespie and Mitsukuri, *THIS JOURNAL*, **44**, 707 (1922).

² Wörmann, *Ann. Physik.* [4] **18**, 775 (1905).

³ Richards and Rowe, *THIS JOURNAL*, **44**, 684 (1922).