[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN]

THE REFRACTOMETRIC ANALYSIS OF SOLUTIONS OF PURE COMPOUNDS

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I. Telluric Acid

Instrumental analysis continues to play an ever increasing role in the field of analytical chemistry. The reason for this probably lies in the fact that it quite often combines a satisfactory degree of accuracy with a substantial saving of time. Some of the methods of instrumental analysis have, in spite of their excellence, gained favor only slowly. Analysis by means of the immersion refractometer may be given as an example. When one reviews the interesting applications of this method of analysis to the determination of the concentration of solutions of pure compounds, its value becomes more apparent. In addition to the analysis of solutions containing only one pure compound as the solute, it has been possible to analyze mixtures of two salts in solution, one known and one of unknown concentration, mixtures of two salts in solution, both of unknown concentration and the mixtures of three salts in solution, one of known and two of unknown concentration.[1] Of equal interest is the application of the immersion refractometer to the analysis of blood serum,[2] sugar solutions, alcohols, oils, fats and waxes. Still wider application of analysis by means of the immersion refractometer is encouraged by the fact that if there is only a very small sample available, the immersion refractometer may be converted into an Abbé of high precision by an auxiliary prism which is provided with the instrument.

No rigorous relationship has been shown to exist between the refractive index and the molecular weight of the solute, the concentration and the temperature.[3] It is therefore necessary to represent the change of refractive index with concentration by such tables as are illustrated by the publications of Wagner.[4]

In this contribution, we are submitting additional data which we hope will give the immersion refractometer still wider application in the laboratory. This is intended for the analysis of solutions of the materials mentioned and not for a ready reference for refractive indices.

Preparation of Materials

Although telluric acid of a high degree of purity can be prepared by the

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[1] J. A. Clemens, *Ind. Eng. Chem.*, **13**, 813–816 (1921).

[2] J. Becka, *Physiol. Chem.*, **121**, 288 (1922).

[3] C. Chéneveau, *Compt. rend.*, **138**, 1493, 1578 (1900); **139**, 361 (1900); *Ann. chim. phys.*, [8] **12**, 145–228, 289–293 (1907).

[4] B. Wagner, "Tabellen, Sonderhausen," sold by Carl Zeiss, Jena, **1907**.

direct application of Staudenmaier's[5] chromic acid oxidation to the nitric acid solution of crude tellurium dioxide, the acid used in this research was prepared from pure elemental tellurium, which in turn was obtained from tellurium basic nitrate and tellurium dioxide.

Tellurium Basic Nitrate.—Crude tellurium dioxide containing about 95% of tellurium dioxide together with sodium sulfate and traces of iron, copper and selenium, was dissolved in concentrated hydrochloric acid. This solution was then saturated with sulfur dioxide and the precipitated selenium removed by filtration. The filtrate was diluted so that the concentration of the hydrochloric acid was 8 to 10% and sulfur dioxide was again passed into the solution until the tellurium was completely precipitated. After washing repeatedly by decantation, the precipitate was transferred to a Büchner funnel and the washing continued until the filtrate was shown to be free of chlorides. The moist tellurium was then dissolved in dilute nitric acid (1:1) and the characteristic crystals of tellurium basic nitrate were obtained by evaporation and subsequent cooling of the saturated solution.

Tellurium Dioxide.—Tellurium basic nitrate was heated at a temperature of 500° for five hours. The material obtained was anhydrous tellurium dioxide of a very high degree of purity.

Elemental Tellurium.—Tellurium dioxide was dissolved in concentrated hydrochloric acid, diluted until the acid concentration was 8–10%, and the solution saturated with sulfur dioxide. The precipitated tellurium was washed by decantation and finally transferred to a Büchner funnel, where it was further washed until free from chlorides. This slightly moist elemental tellurium was used for the preparation of telluric acid without further drying.

Telluric Acid.[5]—Elemental tellurium was dissolved in an excess of dilute nitric acid (1:1). An excess of chromic acid was added and the solution concentrated by evaporation until crystals began to form. Upon cooling this solution the impure brown crystals of telluric acid were deposited. Although eight recrystallizations of the product from distilled water were sufficient to remove the chromic nitrate and free nitric acid, the crystals used were from a portion which had been prepared for conductance measurements and had been recrystallized twenty-four times. The white, air-dried crystals which contained a small amount of occluded water were ground to eighty-mesh and dried further in a calcium chloride desiccator.

Analysis

In order to establish the purity of the dried telluric acid, it was analyzed for water and tellurium. The water content was determined by passing a current of dry air over a weighed sample which was heated at 450° in a porcelain tube. The water which was evolved was collected in a U-tube which contained concentrated sulfuric acid. Tellurium was determined by the Lenher-Homberger[6] method in which elementary tellurium is precipitated from a hydrochloric acid solution of telluric acid by the addition of sulfur dioxide and hydrazine hydrochloride. The following results offer reasonable evidence of the purity of the telluric acid.

Anal. Calcd. for H_6TeO_6: Te, 55.54; H_2O, 23.55. Found: Te, 55.58; H_2O, 23.50.

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[5] Staudenmaier, *Z. anorg. Chem.*, **10**, 189 (1895).

[6] Lenher and Homberger, THIS JOURNAL, **30**, I, 387 (1908).

Method

Since temperature was an important limiting factor in the use of the immersion refractometer, precautions were taken to keep it constant. The refractometric examination of the telluric acid solutions of various concentrations was made in a constant temperature bath at 25 ±0.03°, while the temperature of the room was 22.5 ± 0.3°. In order to correct the scale readings for possible realignment of the prism of the instrument with respect to the scale in the ocular, the zero of the instrument was determined at least once and sometimes twice for each twelve readings. The reference value for distilled water was taken as 13.20 scale divisions at 25°.

Inasmuch as the analysis of the acid indicated that it was relatively pure and free from occluded water, requisite amounts of the dry acid

TABLE I

TELLURIC ACID, H_6TeO_6

The values given in the table were taken from a curve which was prepared by plotting concentraton values against their corresponding scale readings of the immersion refractometer. Zero for distilled water, 13.20 at 25°. Values in grams per 100 cc. of solution.

	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
15	0.656	0.694	0.730	0.768	0.804	0.841	0.878	0.916	0.952	0.990
16	1.026	1.062	1.100	1.136	1.174	1.210	1.246	1.284	1.320	1.358
17	1.394	1.430	1.466	1.502	1.538	1.574	1.610	1.646	1.682	1.718
18	1.754	1.790	1.824	1.860	1.894	1.930	1.966	2.000	2.036	2.070
19	2.106	2.144	2.182	2.220	2.258	2.296	2.334	2.372	2.410	2.448
20	2.486	2.522	2.558	2.594	2.630	2.666	2.702	2.738	2.774	2.810
21	2.846	2.882	2.920	2.956	2.994	3.030	3.066	3.104	3.140	3.178
22	3.214	3.250	3.286	3.322	3.358	3.394	3.430	3.466	3.502	3.538
23	3.574	3.612	3.648	3.686	3.722	3.760	3.798	3.834	3.872	3.908
24	3.946	3.982	4.020	4.056	4.094	4.130	4.166	4.204	4.240	4.278
25	4.314	4.350	4.388	4.424	4.460	4.498	4.534	4.570	4.606	4.644
26	4.680	4.716	4.754	4.790	4.826	4.864	4.900	4.936	4.972	5.010
27	5.046	5.084	5.122	5.160	5.198	5.236	5.274	5.312	5.350	5.388
28	5.426	5.460	5.494	5.528	5.562	5.596	5.630	5.664	5.698	5.732
29	5.766	5.802	5.838	5.874	5.910	5.946	5.982	6.018	6.054	6.090
30	6.126	6.162	6.198	6.234	6.270	6.306	6.342	6.378	6.414	6.450
31	6.486	6.522	6.558	6.594	6.630	6.666	6.702	6.738	6.774	6.810
32	6.846	6.882	6.916	6.952	6.998	7.024	7.058	7.094	7.130	7.164
33	7.200	7.238	7.274	7.312	7.350	7.388	7.424	7.462	7.500	7.536
34	7.574	7.610	7.648	7.684	7.720	7.758	7.794	7.830	7.866	7.904
35	7.940	7.977	8.013	8.049	8.086	8.123	8.159	8.196	8.233	8.269
36	8.306	8.340	8.376	8.412	8.448	8.482	8.516	8.552	8.586	8.622
37	8.654	8.692	8.728	8.766	8.802	8.840	8.878	8.914	8.952	8.988
38	9.026	9.064	9.100	9.138	9.176	9.214	9.250	9.288	9.326	9.362
39	9.400	9.436	9.474	9.510	9.546	9.584	9.620	9.656	9.692	9.730
40	9.766	9.804	9.840	9.878	9.916	9.952	9.990	10.026	10.064	10.102
41	10.140	10.177	10.214	10.250	10.287	10.324	10.360	10.397	10.434	10.470
42	10.506	10.542	10.578	10.614	10.650	10.686	10.722	10.758	10.794	10.830
43	10.866	10.902	10.938	10.974	11.010	11.046	11.082	11.118	11.154	11.190
44	11.226									

were weighed, dissolved in distilled water and diluted to the proper volume in flasks which had been previously calibrated at 25°. It was found that the use of the conventional type of trough did not afford a uniform temperature. Additional circulation was then provided by pumping water from a constant temperature bath through a glass tube which contained a series of openings and was laid on the bottom of the trough. The excess of water was allowed to drain through the overflow. The refractometer was suspended with the prism immersed in the liquid to be examined a few minutes before a reading was attempted. After the instrument had acquired the temperature of the bath, the reading was taken. Each scale reading reported for a single concentration was the mean of several independent settings of the instrument. Each scale reading used to locate a point in the graphical representation of the data was the result of the examination of two independent solutions for each concentration. Between each set of readings, the prism of the refractometer was washed with distilled water and polished with lens paper. Since this operation changed the temperature of the prism, it was again necessary to suspend the instrument with the prism in the liquid to be examined and allow a few minutes for the temperature to become uniform. In the course of the experiments, it was found that two observers using two different instruments for the examination of the same solutions could obtain an agreement of scale readings of ±0.025 scale divisions. An excellent definition of the border was obtained when the temperature of the bath was uniform.

II. Selenious Acid

Preparation of Selenium Dioxide.—Crude selenium dioxide was dissolved in 10% nitric acid and the insoluble material removed by filtration. The solution was evaporated to dryness and the selenium dioxide sublimed by heating the residue in a six-inch evaporating dish and collecting the sublimed oxide on the sides of a five-inch funnel which was placed over the evaporating dish. The sublimation was repeated three times. Due to the hygroscopic character of selenium dioxide, the product always contained a small amount of water but was otherwise pure.

Method of Analysis

The concentration of the stock solution prepared from the selenium dioxide was determined by analysis for elementary selenium. The method used included the conventional separation of elementary selenium by hydroxylamine hydrochloride, filtration, drying the selenium at 105° and weighing as such. The results were calculated in terms of grams of selenium dioxide per hundred cubic centimeters of solution.

Procedure

The manipulation of the refractometer was identical with that already described for telluric acid. Since the solid selenium dioxide has a pronounced affinity for water, it was desirable to prepare the series of solutions from a standardized stock solution rather than attempt to weigh individual samples of selenium dioxide. The stock solution was measured in a calibrated buret and diluted to the desired volume in calibrated flasks at a temperature of 25°.

TABLE II

SELENIOUS ACID

The values given in the table were taken from a curve which was prepared by plotting concentration values against their corresponding scale readings of the immersion refractometer. Values are grams of SeO_2 per 100 cc. of solution.

	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
16	0.758	0.786	0.814	0.843	0.873	0.902	0.932	0.960	0.989	1.019
17	1.048	1.078	1.107	1.136	1.167	1.198	1.229	1.260	1.289	1.319
18	1.348	1.378	1.407	1.437	1.468	1.498	1.529	1.559	1.588	1.619
19	1.649	1.678	1.709	1.740	1.769	1.799	1.828	1.858	1.888	1.918
20	1.948	1.978	2.009	2.040	2.071	2.099	2.127	2.155	2.185	2.214
21	2.242	2.272	2.301	2.329	2.358	2.388	2.419	2.450	2.479	2.508
22	2.538	2.567	2.597	2.627	2.656	2.685	2.715	2.744	2.774	2.803
23	2.833	2.862	2.890	2.920	2.949	2.979	3.008	3.039	3.068	3.098
24	3.127	3.157	3.186	3.216	3.245	3.275	3.304	3.334	3.364	3.395
25	3.423	3.451	3.480	3.508	3.537	3.567	3.596	3.625	3.655	3.684
26	3.714	3.743	3.773	3.802	3.832	3.861	3.891	3.920	3.949	3.979
27	4.008	4.038	4.067	4.097	4.128	4.159	4.189	4.220	4.250	4.279
28	4.310	4.339	4.372	4.403	4.434	4.462	4.491	4.521	4.550	4.579
29	4.609	4.638	4.668	4.697	4.727	4.756	4.786	4.815	4.845	4.874
30	4.905	4.936	4.967	4.997	5.027	5.056	5.086	5.115	5.145	5.174
31	5.204	5.233	5.263	5.292	5.320	5.348	5.376	5.404	5.433	5.460
32	5.489	5.517	5.546	5.576	5.605	5.634	5.664	5.693	5.723	5.752
33	5.780	5.809	5.836	5.865	5.893	5.921	5.950	5.980	6.009	6.038
34	6.068	6.097	6.125	6.154	6.182	6.210	6.238	6.268	6.295	6.325
35	6.353	6.381	6.410	6.440	6.468	6.496	6.525	6.555	6.584	6.614
36	6.643	6.673	6.701	6.729	6.758	6.788	6.817	6.843	6.876	6.906
37	6.935	6.964	6.994	7.023	7.053	7.082	7.112	7.141	7.171	7.200
38	7.230	7.259	7.289	7.318	7.347	7.377	7.407	7.436	7.464	7.492
39	7.522	7.551	7.580	7.610	7.640	7.669	7.698	7.728	7.757	7.787
40	7.816	7.846	7.875	7.905	7.934	7.963	7.993	8.022	8.052	8.081
41	8.111	8.140	8.170	8.199	8.229	8.258	8.288	8.317	8.346	8.375
42	8.405	8.435	8.462	8.494	8.523	8.553	8.582	8.612	8.641	8.671
43	8.700	8.730	8.759	8.788	8.818	8.847	8.877	8.906	8.936	8.965
44	8.995	9.024	9.054	9.083	9.113	9.142	9.172	9.201	9.230	9.260
45	9.289	9.319	9.348	9.378	9.407	9.437	9.466	9.496	9.525	9.555
46	9.584	9.614	9.643	9.672	9.702	9.731	9.761	9.790	9.820	9.849
47	9.880	9.911	9.940	9.970	9.999	10.030	10.060	10.090	10.120	10.150
48	10.180	10.209	10.238	10.267	10.297	10.326	10.356	10.385	10.415	10.444
49	10.474									

III. Potassium Ferrocyanide

Preparation and Analysis.—Ordinary "chemically pure" potassium ferrocyanide was recrystallized three times from aqueous solution and the resulting product pulverized and finally dried in a calcium chloride desiccator. The dry material was then analyzed for potassium and iron.

Potassium.—A 0.5g. sample was digested with concentrated sulfuric acid until the cyanide was destroyed. The sample was treated with water until the acid strength was about 10% and the iron was removed by double precipitation with ammonium hydroxide. The combined filtrates from the precipitated ferric hydroxide were evaporated to dryness and the residue was heated at 450°. The resulting potassium sulfate was weighed and the results were calculated to per cent. of potassium.

Iron.—For this determination the sample was dissolved in 10% sulfuric acid and the ferrous iron titrated with $N/10$ potassium permanganate, following the details of the potentiometric method described by Kolthoff,[7] and Hostetter and Roberts.[8]

Anal. Calcd. for $K_4Fe(CN)_6$: K, 42.46; Fe, 15.16. Found: K, 42.40; Fe, 15.13.

Procedure

Solutions of the concentrations desired were prepared by dissolving weighed samples of the dry material in water and diluting to the proper volume in calibrated flasks, maintaining the temperature at 25°. The same precautions were followed in the use of the refractometer as have been described for telluric acid.

TABLE III

POTASSIUM FERROCYANIDE—$K_4Fe(CN)_6$

Scale reading	G. of $K_4Fe(CN)_6$ in 100 cc. of solution	Scale reading	G. of $K_4Fe(CN)_6$ in 100 cc. of solution	Scale reading	G. of $K_4Fe(CN)$ in 100 cc. of solution	Scale reading	G. of $K_4Fe(CN)_6$ in 100 cc. of solution
15.7	0.466	36	4.388	56	8.302	76	12.236
17.0	0.704	37	4.584	57	8.496	77	12.432
18	0.898	38	4.774	58	8.692	78	12.620
19	1.092	39	4.964	59	8.888	79	12.808
20	1.286	40	5.154	60	9.086	80	13.004
21	1.480	41	5.334	61	9.284	81	13.200
22	1.674	42	5.540	62	9.484	82	13.388
23	1.868	43	5.736	63	9.684	83	13.576
24	2.058	44	5.934	64	9.882	84	13.764
25	2.256	45	6.132	65	10.080	85	13.968
26	2.448	46	6.330	66	10.276	86	14.164
27	2.640	47	6.528	67	10.472	87	14.360
28	2.834	48	6.728	68	10.668	88	14.552
29	3.028	49	6.928	69	10.864	89	14.744
30	3.222	50	7.128	70	11.060	90	14.938
31	3.416	51	7.328	71	11.256	91	15.132
32	3.610	52	7.524	72	11.452	92	15.324
33	3.804	53	7.718	73	11.648	93	15.516
34	3.998	54	7.914	74	11.844		
35	4.192	55	8.108	75	12.040		

Discussion

The results recorded were obtained by the graphical method of interpolation. Scale readings were plotted against concentrations, the concentration being given in terms of grams of solute per 100 cc. of solution.

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[7] Kolthoff, *Rec. trav. chim.*, **41**, 343 (1922).

[8] Hostetter and Roberts, THIS JOURNAL, **41**, 1337 (1919).

Forty to fifty points were plotted to establish the slope of each curve. In the range of concentrations given in the tables, there are no apparent irregularities. A change of concentration of telluric acid corresponding to 0.1 of a unit in scale divisions is equivalent to about 0.037 g. per 100 cc. of solution. Likewise for selenious acid, a change of concentration corresponding to 0.1 of a unit in scale divisions is equivalent to 0.029 g. of selenium dioxide per 100 cc. of solution. For potassium ferrocyanide, 0.1 of a unit in scale divisions is equivalent to 0.019 g. of the salt per 100 cc. of solution. As has been previously noted, two individuals can obtain readings whose mean values are within a range of ±0.025. It is therefore believed that a proper control of the method assures rapid analysis with reasonable precision for solutions of the materials mentioned.

The writers wish to acknowledge the kindness of Bausch and Lomb in providing one of their new instruments for this work.

Summary

1. The results in Table I correlate the scale readings of an immersion refractometer and the concentration of aqueous solutions of telluric acid thus making possible a rapid and reasonably accurate determination of the concentration of telluric acid solutions of unknown strength.

2. The results in Table II for selenious acid and those in Table III for potassium ferrocyanide also afford a rapid and accurate means of determining the concentration of these solutions.

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[Contribution from the Chemical Laboratories of Stanford University]

THE INCOMPATIBILITY BETWEEN ANY THEORY OF COMPLETE DISSOCIATION AND MIGRATION DATA FOR DIVALENT IONS

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In 1814 Porrett electrolyzed solutions of mixtures of "prussides" and observed that the potassium and the iron moved in opposite directions, the iron going toward the anode. Ever since, the ferrocyanide ion has been the model of a complex anion. The use of migration is, on account of its simplicity and unambiguity, one of the most powerful tools of the physical chemist in the cases where it can be applied. We wish to adduce it in deciding the rival claims of incomplete and complete dissociation in solutions containing divalent ions.

The object of this communication is to present experimental data which show that all divalent ions take part to a certain extent in such phenomena as those illustrated in extreme form by the prussides above, and familiar to us since Hittorf in the behavior of cadmium iodide. The new data