PROBLEMS AND EXPERIMENTS IN

INSTRUMENTAL ANALYSIS

Clifton E. Meloan
Robert W. Kiser

PROBLEMS AND EXPERIMENTS IN INSTRUMENTAL ANALYSIS

CLIFTON E. MELOAN AND ROBERT W. KISER

Assistant Professors of Chemistry
Kansas State University

CHARLES E. MERRILL BOOKS, INC.
1300 Alum Creek Drive, Columbus 16, Ohio

PERIODIC CLASSIFICATION OF THE ELEMENTS

(Based on $C^{12} = 12.0000$)

1961 Atomic Weights

1 H 1.0080	2 He 4.003																2 He 4.003
3 Li 6.939	4 Be 9.012											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.9994	9 F 18.998	10 Ne 20.183
11 Na 22.990	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.102	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (99)	44 Ru 101.1	45 Rh 102.90	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	57 to 71	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 197.0	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.05	89 to 103															

Lanthanide series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide series	89 Ac (227)	90 Th 232.04	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (249)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lw (257)

FOUR PLACE TABLE OF COMMON LOGARITHMS

N	0	1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996
N	0	1	2	3	4	5	6	7	8	9

PREFACE

Our purpose in writing this laboratory manual has been twofold. First, we wished to present a series of experiments which would illustrate the principles, scope and limitations of the instrumentation utilized in solving analytical problems in modern chemical research, and second, we wished to show the student in a reasonably simplified manner how various physical constant, structure analysis, and quantitative information might be determined from the data obtained using these instruments. One of the significant advantages of instrumental methods of analysis over the "wet" methods is that the chemical composition is determined by measuring specific physical properties of the system being studied. Because of this, the instrumentation is used not only in analytical determinations, but also in various aspects of chemical research wherein the physical properties of materials of known composition are to be determined. Although we have emphasized the analytical aspects of the various instrumental methods considered in this laboratory manual, we have also attempted to show some important uses of the same instrumentation in chemical research.

This manual is intended to complement the many fine texts currently available. Most instrumental texts primarily emphasize the analytical applications and do not stress other areas which may be of value to the physical, organic, and inorganic chemists, and others. We have attempted to reduce these limitations by including both experiments and problems in many of these areas.

The experiments are presented in such a way as to avoid the "cook-book" style as much as possible. If laboratory work is approached in a "cook-book" manner, and the student carries out the experiments in only a mechanical way, he will derive little benefit from them. On the other hand, if suitable directions are not supplied, the student may wander aimlessly in the laboratory; it is conceivable that serious damage might also be done to certain expensive instrumentation if no directions are given. In this manual, no explicit instructions as to which knob to turn or which button to push are given. With the wide variety of instruments available for each technique, a separate set of instructions would be necessary for each instrument. We believe this to be not only undesirable but unnecessary, for we know of no instructor who would introduce students to scientific equipment without first explaining its operation in detail. However, once this explanation of the operation of the instrumentation has been given, the student is able to proceed as directed by these experiments. The instructor is therefore free to explain the details of other equipment to other students in the class. This is a necessity since there is seldom sufficient equipment to allow each student in the class to carry out individually the same experiment at the same time.

Because of this necessary lack of equipment, students are often required to do laboratory work which has not previously been discussed in the lecture portion of the instrumental analysis course. As a result we have included in certain cases a brief explanation of the principles involved. The decision concerning how much material of an informational or explanatory nature to include with the experiments and problems has not been completely arbitrary; we have attempted to give the principles and basic information necessary to solve the problems, which are generally illustrative of typical information which the experimental data may yield. But the desired length of this volume dictated that this not be an exhaustive treatment. Certainly the instructor will supply much more information with the principles in the classroom.

The choice of topics has been influenced by those techniques frequently employed in analytical problems. Although paper and column chromatography are not instrumental in nature, they have been included because of their value to students of disciplines closely related to chemistry. Statistical analysis is not itself an instrumental method, but has been included in this volume to emphasize that the laboratory worker must understand the meaning, limitations, and precision of his accumulated data. The selection and design of experiments were made so as to amplify the applications of the technique and the physical principles of the method. The number of experiments is sufficiently large so that the individual instructor may select experiments which may be performed with the equipment available to his classes.

If there is one feature wherein we believe all instrumental texts present some evidence of inadequacy, it is in the treatment of problems. It is true that there are many problems in most texts, but there is often little if any explanation of how to solve these problems. One of the current trends in analytical chemistry is toward presenting a one-semester course in instrumental analysis to the undergraduate students in their junior or senior year. There is also an increasing awareness of the importance of many of these instrumental techniques by departments outside of chemistry, such as agriculture, milling, home economics, and the natural sciences. The number of students with inadequate mathematical preparation taking a course of this type in instrumental analysis is increasing. Step-by-step explanations of how to solve problems not only helps these students but it may also free the instructor to devote more time to the theory and principles involved. Several associated problems of each type are included at the end of each chapter. This permits the instructor to assign different problem sets for several semesters without duplication.

With but a single exception, we have throughout this volume employed oxidation potentials. In the treatment of chronopotentiometry in Chapter 24, we have used reduction potentials. The signs of the electrode potentials we have used are those commonly employed in courses which are prerequisite to the instrumental analysis course; it is for this reason we have deviated from the recommendations promulgated for the signs of electrode potentials. As the student becomes well-acquainted with the principles, we believe the problem of the sign of the potential will be less serious.

We are grateful to W. Baitinger, V. Cates, and D. Gere for assistance in checking various experiments and for reading portions of the original manuscript, as well as to our colleagues at Kansas State University for their support. Thanks are also due to Miss Marlene Besack and Mrs. C. E. Meloan who typed various copies of the manuscript. It is a distinct pleasure for us to acknowledge the helpful criticisms of the reviewers, including Professor Robert L. Pecsok of the University of California, Professor John G. Mason of Virginia Polytechnic Institute, Professor Harold F. Walton of the University of Colorado, and Professor John T. Stock of the University of Connecticut. Especial appreciation is due our wives, Marilyn Meloan and Barbara Kiser, for their understanding and encouragement during the preparation of this volume.

The authors would greatly appreciate the aid of those using this book in calling our attention to any errors, so that corrections may be made in future printings.

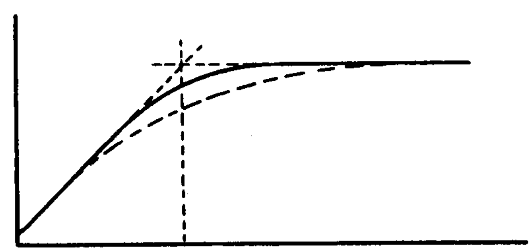
Manhattan, Kansas

Clifton E. Meloan
Robert W. Kiser

CONTENTS

ERRATA PROBLEMS AND EXPERIMENTS IN INSTRUMENTAL ANALYSIS

Page vii	Exp. No. 12; solution should be solutions.
Page x	Exp. No. 49; Hg_2SO_4 rather than Hg_2SO_3.
	Exp. No. 51; remove the comma after of.
Page xi	Exp. No. 66; Ferrous should be ferrous.
Page xii	Chapter 23, part B; Titration should be titrations.
Page xiii	Chapter 27, part C; Van Deempter not Von Deempter.
	Exp. No. 89; glutamic acid not glutomic acid.
Page 7	1st column last set of equations; change $50C_p$ to $50C_t$ in both instances.
Page 8	The dotted line in figure 2-1 is missing.



Page 21	2nd column 5th line from the bottom; change 0.28 to 1.28.
Page 25	Example 2, 2nd equation; add (1.3×10^{-3}) to the denominator.
Page 29	Problem 5; add $a_m = 2.3 \times 10^4$
Page 43	Column 2; change θ to 0 in $\theta = A \log 360 + B$
Page 55	Figure 9-1; change all hv's to $h\nu$'s
Page 56	After equation 9-4; the units of $\nu 1$, $\nu 2$ and $\Delta\nu$ are sec-1.
Page 75	Column 1 2nd line of par 1; make the last the a then.
Page 76	Column 2 line 2; molybdenum
Page 88	Problem 13; should be at the 95% confidence level.
Page 105	Figure 13-7; the bonds between the H's and the rest of the molecule are missing.
Page 111	Method 2; change 1931 to 1921.
Page 114	Exp. 38 line 8; change 1931 to 1921.
Page 115	Last line column 1; change 3,5 to 2,5.
Page 117	Figure 15-1; delete the strong lines between the three $C\text{-}CH_3$ groups and the $C\text{-}CH_2CH_3$ group and replace them with dashed lines.
Page 181	Figure 22-4; i_d at 0.84v; change 8.6 to 11.6.

Page 185 Figure 22-7; 0.0 on the Y axis should be below on the X axis. Each division on the Y axis = 10 mm.

Page 190 Exp. 75 part 1a; 0.05M should be 0.005M.

Page 190 Figure 23-2; remove the horizontal connecting line just below the 1.5v source.

Page 202 Figure 24-7; change $\frac{1}{2}$ inch = 1 sec to 1 square = 1 sec.
Problem 16 line 5; it should be E $\widehat{\frac{1}{2}}$

Page 206 Column 2 line 4; should be Table (25-1).

Page 214 & 215 Example 1. Change 0.6121 to 0.6021 (4 times).

Page 220 Equation 27-23; change $-)2^2$ to $-2)^2$.

Page 263 Column 2 line 4; change soils to coils.

Page 264 Example 2 line 2; nucleus.

Page 267 Equation 30-21; add (before $2n_1I_1$

Page 269 1st column equation 30-29; change 10,000 to 10.000
2nd column Example 7; add square root sign to $P = \sqrt{}$

In addition the credit lines for the following figures are missing.

Page 32 Figures for Exp. 6-19 and 6-20 are courtesy of the American Petroleum Institute.

Pages 35, 34, 36, & 37; All figures are courtesy of the Sadtler Laboratories.

Page 61; Top figure and 3rd figure; courtesy of the American Petroleum Institute.
2nd and bottom figure; courtesy of Sadtler Laboratories.

Page 62 Top figure; courtesy of American Petroleum Institute.
Lower figure; courtesy of Sadtler Laboratories.

Page 63 Top figure and both figures of problem 15, 16 and 17. courtesy of American Petroleum Institute.
2nd figure from the top. courtesy of Sadtler Laboratories.

Page 114 Figure 14/3 and 14-4; Courtesy of Howard Strobel, Chemical Instrumentation, Addison Wesley Publishing Co. Reading Mass., 1960.

Page 125 & 126. Figures 16-1 and 16-2; Courtesy of Leeds and Northrup Co.

Page 284 Appendix ii. Courtesy of N.B. Colthup *chapter 1*

COLORIMETRY

Of all the simple color comparators, the Duboscq colorimeter is probably the most widely used. Its operation is based upon a variable depth principle in which the color of a standard solution is matched to the color obtained by an unknown. When such a match is obtained the concentration is calculated based upon the following relationships:

$$b_{std}\,c_{std} = b_{unk}\,c_{unk}. \qquad (1\text{-}1)$$

where b = cell thickness
c = concentration

This is derived from the Beer-Bouger Law in the following manner:

$$A = abc \qquad (1\text{-}2)$$

where A = absorbance
a = absorption coefficient
b = cell thickness
c = concentration

Such a relationship will exist both for the standard solution and the unknown solution. When a color match is obtained, both solutions are absorbing an equal amount of radiation. Thus

$$A_{std} = a_{std}\,b_{std}\,c_{std} = A_{unk} = a_{unk}\,b_{unk}\,c_{unk} \qquad (1\text{-}3)$$

or

$$a_{std}\,b_{std}\,c_{std} = a_{unk}\,b_{unk}\,c_{unk} \qquad (1\text{-}4)$$

If the solutions have nearly the same concentration so that their hues are the same, then a_{std} = a_{unk}; that is, both solutions will absorb the same amount per unit cell thickness. This gives

$$b_{std}\,c_{std} = b_{unk}\,c_{unk} \qquad (1\text{-}5)$$

and it is seen that the product of the concentration times the cell thickness of the standard must equal the same product for the unknown.

EXAMPLE 1

A 0.200 g sample of steel was weighed, dissolved in acid, the manganese oxidized to permanganate and the sample diluted to 100 ml. 25 ml of 0.008 N $KMnO_4$ (standardized against iron wire) was diluted to 100 ml in a volumetric flask and used as a standard solution in a Duboscq colorimeter. Both cups were filled with the standard solution; the average reading for the right hand cup was 32.0 mm and for the left cup it was 31.7 mm. The standard solution was left in the left cup with the 31.7 mm setting and the solution in the right cup was replaced with the diluted steel sample which produced an average reading of 28.3 mm. Calculate the percent manganese in the steel.

The concentration of the standard solution is obtained based upon the fact that the number of meq of $KMnO_4$ present before dilution equals the number of meq present after dilution. Since the number of meq = (ml) (N) we have:

$$(25)(0.008) = (100)(N) \text{ or } 0.002\text{ N}.$$

The values of b_{std} and b_{unk} are arrived at in this manner. Since it is difficult to obtain cells and optics for instruments of this type that match each other perfectly, a correction factor must be obtained. From the data it appears that the right cup reads 0.3 mm higher than the left cup when both contain the same solution.

This problem is eliminated in a manner similar to that employed in substitution weighing where both the object and the weights are balanced against the same vial of shot. Here, both the known and the unknown are placed successively in one cup (right) and matched against the other reference (left) cup. This effectively cancels any differences in optics which are present. From equation (1-5);

$$(32.0)(0.002) = (28.3)(N)$$

$$N = 0.00226$$