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Relatório de Estágio

Da Engenheira Química

Gloria Berenice C.T.C.Brazão da Silva

Rio, 8 de julho de 1975

Gloria Berenice C.T.C. Brazão da Silva

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1 - Introdução

O presente relatório descreve a viagem empreendida pela autora aos Estados Unidos da América incluindo comparecimento a congresso e principalmente estágio em laboratórios de espectrografia de emissão.

Cronograma da viagem

28/2/75 - 6ª feira - Partida do Rio de Janeiro

1/3/75 - sábado - Chegada a New York

2/3/75 - domingo - Chegada a Cleveland
Inscrição na "26th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy"

3/3/75 - 7/3/75 - Participação na "26th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy" realizada no Cleveland Convention Center

8/3/75 - sábado - Partida para Boston

9/3/75 - domingo - Boston

10/3/75 a 11/3/75 - Visita à fábrica de espectrógrafos Jarrell-Ash

11/3/75 - 3ª feira - Partida para Washington, DC

12/3/75 a 21/5/75 - Estágio nos laboratórios de espectrografia de emissão do United States Geological Survey, em Reston

22/5/75 - 5ª feira - Providências para viagem de volta ao Brasil, junto ao U.S.G.S. e à U.S.A.I.D., em Washington, DC

23/5/75 - 6ª feira - Chegada a New York
Partida para o Rio de Janeiro

24/5/75 - sábado - Chegada ao Rio de Janeiro

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2. Objetivos do Estágio

O constante aprimoramento e a introdução de novas técnicas nos laboratórios de espectrografia de emissão da C.P.R.M. constituiram o objetivo básico de minha viagem aos Estados Unidos. Neste, três pontos importantes podem ser destacados:

2.1 - Utilização do "laser microprobe" na identificação mineralógica;

2.2 - Comparecimento à "26th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy", na qual, ao lado da apresentação de trabalhos de qualidade destaca-se renomada exposição de instrumental;

2.3 - Estudo da técnica de espectrografia de emissão quantitativa e de técnicas especiais.

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3. Trabalhos Realizados no Estágio

3.1 - Laboratórios da Jarrell-Ash, Divisão da Fisher Scientific Company: análise espectrográfica qualitativa utilizando o "laser microprobe";

3.2 - Laboratórios do United States Geological Survey:

3.2.1 - Análise quantitativa utilizando espectrografia de emissão;

3.2.1.1 - Preparação e seleção de padrões;

3.2.1.2 - Densitometria e métodos de calibração;

3.2.1.3 - Curvas analíticas e seleção de raias;

3.2.2 - Métodos especiais de análise quantitativa utilizando espectrografia de emissão para determinação de:

3.2.2.1 - chumbo em zircão;

3.2.2.2 - rubídio, césio e lítio;

3.2.2.3 - elementos voláteis para a espectrografia de emissão;

3.2.2.4 - terras raras;

3.2.3 - Análise espectrográfica semiquantitativa de grão;

3.2.4 - Introdução ao método de análise espectrográfica semiquantitativa utilizando computador.

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4. Contatos Mantidos

Além dos contatos mantidos com os técnicos da Jarrell-Ash para discussão de detalhes de funcionamento do "laser micro probe" de que dispomos na DIESPE, e, com os técnicos do U.S. Geological Survey para discussão de métodos de trabalho para análise de material geológico utilizando espectrografia de emissão, tive a oportunidade de visitar grande número de "stands" de firmas especializadas em material espectrográfico na "26th Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy". Devo frisar que os contatos nunca foram unilaterais. Houve sempre grande interesse e alguma surpresa, sempre positiva, quando tomavam conhecimento do alto nível do trabalho realizado pela C.P.R.M. e das instalações do LAMIN, reveladas pela propaganda do mesmo distribuida por mim na ocasião.

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5. Análise Crítica do Estágio

O programa de estágio esteve de acordo com os objetivos propostos e todo o tempo disponível foi utilizado de maneira eficiente e racional, o que pode ser constatado pela análise dos ítens 1, 2 e 3. Todas as informações solicitadas foram fornecidas e a discussão de problemas técnicos com pessoal de alto nível sempre possível, tanto na Companhia Jarrell-Ash quanto nos laboratórios do U.S. Geological Survey.

A participação na "26th Pittsburgh Conference" foi muito proveitosa porque pude assistir à apresentação de trabalhos de gabarito e ver o que de mais moderno existe no campo do instrumental espectrográfico.

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6. Conclusões

De um modo geral, e como já tive oportunidade de verificar em estágio anterior, os métodos de trabalho utilizados no LAMIN para análise espectrográfica de emissão semiquantitativa estão de acordo com os empregados pelos laboratórios do U.S.G.S. e laboratórios particulares, como os da Jarrell-Ash.

Com a obtenção da informação técnica já referida nos ítens anteriores, considero que a DIESPE poderá, em futuro bem próximo, iniciar uma programação de trabalho em que se utilizem o "laser microprobe" e técnicas de análise espectrográfica quantitativa.

Acredito que, dentro de mais algum tempo e com um maior volume de trabalho, seja de interesse para a CPRM a utilização do sistema de análise espectrográfica utilizando computador, sistema este que existe no momento apenas nos laboratórios do USGS em Reston, e que está agora sendo instalado nos laboratórios do USGS em Denver.

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7. Recomendações

Para dar início ao esquema de trabalho proposto no ítem das conclusões, necessita o LAMIN adquirir material fotográfico especial e alguns acessórios para o instrumental existente na DIESPE, sendo esta no entanto uma aquisição de pequena monta.

A continuação do relacionamento com outros laboratórios, como os do USGS, será de grande importância, considerando as vantagens decorrentes de troca de informação técnica efetuada em viagens ao exterior.

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8. Agradecimentos

Agradeço ao U.S.G.S., à U.S.A.I.D. e à Jarrell-Ash, o bom acolhimento que me foi dispensado.

Agradeço também à C.P.R.M. a oportunidade que me foi dada de tomar conhecimento dos mais recentes progressos no campo da espectrografia de emissão.

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9. Anexos

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SPECTROCHEMICAL COMPUTER ANALYSIS—ARGON-OXYGEN D-C ARC METHOD FOR SILICATE ROCKS

By A. F. DORRZAPF, JR., Washington, D.C.

Abstract.—Use of an argon-oxygen atmosphere eliminates the interference of cyanogen bands with many sensitive analytical lines. The jet-controlled atmosphere also improves the stability of the arc. These procedural changes, coupled with computerized analysis of the spectra, result in increased detectability, precision, and speed as compared to the former visual semiquantitative technique.

Complete spectrochemical analysis of geologic materials by a recording system and computer was developed by Helz, Walthall, and Berman (1969). There has been a concerted effort in the U.S. Geological Survey laboratories since then to improve and extend the capability of this method. The improved system, the procedural part of which is described in this paper, is now in routine service.

Basic changes in the recording system have been described by Helz (1973). The previous system used two 102- by 254-mm (4- by 10-inch) plates to cover the entire wavelength range. Two recordings were, therefore, required for each sample spectrum. This procedure, moreover, necessitated fiducial lines for each plate as well as massive computer storage for a complete analysis. The conversion to 102- by 508-mm (4- by 20-inch) plates allows continuous recording of a spectrum from 2300 to 4700 A, uses only two fiducial lines, simplifies computer processing, and reduces storage requirements.

Although the conversion to 508-mm plates provided continuity of recording, the cyanogen band region (3500–4216 A) was still of limited use for analyses. The intensity of these bands was reduced considerably by use of an argon-oxygen atmosphere during excitation. An additional advantage of this atmosphere is better arc control.

Acknowledgments.—The author gratefully acknowledges the guidance and assistance of Armin W. Helz and the cooperation and assistance of other colleagues, in particular Sol Berman and Frank G. Walthall.

EXPERIMENTAL METHOD

The basic guideline for this work was to keep the method simple, rapid, and as sensitive for trace and minor elements as the semiquantitative method of Myers, Havens, and Dunton (1961). To eliminate cyanogen bands, an atmosphere can be introduced around the electrodes by using some type of jet. The jet designed by Helz (1964) was preferred over the Stallwood model (Stallwood, 1954) because no glass dome is required on the Helz jet, thus eliminating cleaning of the dome between exposures. Various atmospheres have been used to eliminate cyanogen bands (Thiers, 1953; Thiers and Vallee, 1957; Shaw and others, 1958). After investigating many of these gases and combinations of argon and oxygen, we chose a mixture of 70 percent argon and 30 percent oxygen at a flow rate of 6.6 l/min.

It was necessary to increase the size of the sample used in the semiquantitative procedure from 10 mg of sample and 20 mg of graphite to 15 mg of sample and 30 mg of graphite to maintain the desired sensitivity for all elements. In addition, an increase of the initial burning time, at 5 amp, from 10 to 20 sec maintains the sensitivity for volatile elements. The details of excitation and other spectrographic conditions follow:

Electrodes: Cathode, ASTM type C-6, 2 in. long; anode, ¼-in. diam thin-walled graphite (Ultra No. 3170).
Electrode charge: 15 mg sample + 30 mg graphite (type UCP-2/200 mesh).
Spectrograph: 3.4 m Ebert design (Mark III).
Power source: 325 v open circuit d-c arc, resistance controlled.
Excitation: 15 amp d-c arc set with empty graphite electrodes.
Arc gap: 4 mm, maintained throughout burn.
Exposure: 20 sec at 5 amp followed by 130 sec at 15 amp, continuous burn.
Atmosphere: 70 percent argon + 30 percent oxygen; 6.6 l/min flow rate with top of Helz jet nozzle 2 mm below top of electrode.
Wavelength range: 2300–4700 A; first order.
Grating: 600 groove/mm; 5 A/mm reciprocal linear dispersion.
Slit: 25 μm wide and 2 mm high.
Filter: 47-percent transmission neutral-density filter.
Illumination: Arc image focused on collimator by 450-mm focal-length lens at slit.
Mask at collimator: 1.8 cm.
Emulsion: Kodak III-0 (102- by 508-mm plates).
Processing: Kodak D-19 developer, 3¼ min at 20°C; Kodak indicator stop bath, 30 sec; Kodak fixer, 8 min; wash, 20–30 min at 20°C; and dry with warm air for 20 min.

Six-step standards are prepared as described by Myers, Havens, and Dunton (1961). All standards and samples are weighed, mixed with graphite, and loaded into the electrode in

Table 1.—*Spectral lines used in spectrochemical computer analysis, listed in order of sensitivity*

Element	Wavelength (angstroms)	Concentration limits (percent)
	3280.683	0.000010– 0.000681
	3382.891	.000010– .00100
	2660.393	0.0316 – 0.464
	2378.408	.215 – 2.15
	2669.166	2.15 –31.6
	2860.452	0.0100 – 1.00
	2349.84	.316 – 1.00
	2370.77	.215 –10.0
	2369.67	.215 –10.0
	2675.95	0.000681– 0.0147
	2427.95	.00100 – .0681
	3122.781	.00215 – .100
	2496.778	0.00100 – 0.0215
	4554.042	0.000100– 0.00147
	4130.664	.00147 – .0464
	3071.591	.0100 – .215
	2348.610	0.000100– 0.00464
	3321.343	.000100– .0100
	3321.086	.000215– .0147
	3067.716	0.000100– 0.0100
	2897.975	.00215 – .100
	3024.635	.0100 – .215
	2997.314	0.0681 – 3.16
	2721.645	.464 –31.6
	3274.661	1.00 –31.6
	3261.057	0.00147 – 0.0464
	3465.201	.00464 – .0681
	4165.606	0.00200 – 0.136
	3201.714	.00431 – .431
	3453.505	0.000100– 0.00464
	3449.170	.000100– .0215
	3412.633	.000464– .0215
	3593.488	0.000100– 0.00100
	4254.346	.000100– .00215
	3024.350	.000464– .0681
	2843.252	.000464– .100
	2731.908	.0100 – .681
	4555.355	0.316 – 1.47
	4593.177	1.00 – 4.64
	3247.540	0.000100– 0.000681
	3273.962	.000215– .00100
	2824.369	.00464 – .100
	3407.80	0.000316– 0.0316
	4211.719	.000316– .0147
	3319.887	.00100 – .100
	3230.585	0.000215– 0.0316
	3220.730	.000681– .100
	4129.737	0.000100– 0.00316
	4205.046	.000100– .00316
	2906.676	.000681– .100
	2813.95	.00100 – .100
	2727.780	.00316 – .100
	3175.447	0.0506 – 5.06
	2391.474	.506 –23.5
	2385.007	1.09 –23.5
	2943.637	0.000215– 0.00316
	2944.175	.00147 – .100
	3549.365	0.000316– 0.0215
	3331.388	.00215 – .100
	2651.178	0.000100– 0.0215
	2651.575	.00464 – .0681
	3269.494	.00464 – .0681
	2916.481	0.00100 – 0.464
	3109.117	.00464 – .681
	2866.373	.00681 – .681
	2536.519	0.0147 – 2.15
	3131.833	.464 – 4.64
	3456.00	0.000100– 0.00681
	3398.98	.000316– .0147
In	4511.323	0.000464– 0.00681
	3039.356	.000464– .0147
Ir	3220.780	0.000681– 0.100
	2849.725	.00464 – .215
K	4044.140	0.0681 – 0.681
	4047,201	.147 – 1.00
	3446.372	1.00 –10.0
La	3245.120	0.00147 – 0.147
Li	3232.61	0.00316 – 0.215
	4273.28	.316 – 1.47
	3985.79	.464 – 4.64
Lu	2911.39	0.000316– 0.0464
Mg	2779.834	0.00215 – 0.0681
	2776.690	.00215 – .215
	2782.974	.00215 – .316
	2781.417	.00464 – .316
	3336.680	.00464 – .316
	2798.06	.00681 – .681
	3329.930	.0100 – 2.15
	2936.537	.0316 – 2.15
	2938.538	.100 – 6.81
	4571.15	1.47 –30.0
Mn	2798.271	0.000100– 0.0100
	2801.064	.000100– .0147
	2949.205	.000316– .0316
	4502.220	.00681 – .681
	3070.266	.00681 – 1.00
	3629.741	.0147 – 1.00
	2914.603	.0147 – 1.47
	2626.640	.215 – 4.64
	2715.551	.681 –10.0
	2387.02	4.64 –46.4
Mo	3864.110	0.000100– 0.00215
	3170.347	.000147– .0147
	3193.973	.000215– .0147
	2816.154	.00215 – .100
Na	3302.323	0.00464 – 0.147
	3302.988	.00681 – .316
	2853.031	.0681 – 4.64
	2852.828	.215 – 6.81
Nb	3163.402	0.000215– 0.0681
	3194.977	.000464– .100
Nd	4303.573	0.00147 – 0.0464
Ni	3492.956	0.000100– 0.00215
	3101.879	.000464– .0316
	2943.914	.00147 – .100
Os	3301.559	0.000100– 0.100
	2909.061	.00215 – .147
P	2554.93	0.0464 – 4.64
Pb	2833.069	0.000100– 0.0681
	2663.166	.00681 – .100
	2873.316	.0147 – .100
	2393.794	.0681 – 4.64
Pd	3404.580	0.000022– 0.00147
	3242.703	.000068– .00464
	3516.943	.000215– .00681
Pr	3908.431	0.000215– 0.00681
	4222.98	.00147 – .0316
	3121.571	.0316 – .100
Pt	2997.967	0.000681– 0.0464
	2659.454	.000681– .0681
	2830.295	.00215 – .100
Rb	3591.59	1.47 –10.0
	3348.72	3.16 –10.0
Re	3460.47	0.00100 – 0.0464
	3464.722	.00215 – .0681
Rh	3434.893	0.000010– 0.00147
	3692.357	.000100– .00147
	3396.85	.000147– .00464
	3502.524	0.000215– 0.00681
	3462.040	.000681– .0147
Ru	3498.942	0.000046– 0.00464
	3436.737	.000100– .0100
	2988.948	.00147 – .147
Sb	2598.062	0.00681 – 0.100
	2877.915	.00681 – .147
	3267.502	.0100 – .316
	2670.643	.100 – 2.15
	2445.515	.215 – 6.81
	2383.63	1.00 – 6.81
Sc	3911.810	0.000100– 0.00215
	4246.829	.000100– .00316
	3353.734	.000100– .00681
Si	2519.207	0.00316 – 0.100
	2987.648	.0147 – .681
	2452.136	.100 –14.7
	2577.13	2.15 –34.3
Sm	4296.750	0.000464– 0.00464
	3408.668	.00316 – .100
Sn	3175.019	0.000316– 0.0147
	3034.121	.000316– .0215
	2839.989	.00100 – .0215
	2863.327	.00681 – .0316
Sr	4077.714	0.000046– 0.000215
	4607.331	.000100– .00215
	3464.457	.00147 – .0464
	4161.796	.00464 – .147
	2931.830	.0681 – 6.81
	3569.469	1.00 –46.4
	2428.095	2.15 –46.4
Ta	3311.162	0.0147 – 1.00
	2714.674	.0316 – 1.00
Tb	3293.07	0.00147 – 0.100
	4278.51	.00464 – .100
Te	2385.76	0.0316 – 1.00
Th	4116.718	0.00215 – 0.215
	4069.210	.0100 – .316
	2837.299	.0100 – .464
	2870.413	.0147 – .681
Ti	3199.915	0.000464– 0.0464
	3186.454	.000464– .100
	2641.099	.0100 – .316
	2644.264	.0681 – .681
	2679.926	.100 – 6.81
Tl	3775.72	0.000316– 0.00681
	3519.24	.00147 – .0147
	2767.87	.00147 – .100
	3529.43	.00681 – .100
	3229.75	.100 – .681
Tm	3462.20	0.000316– 0.0100
	4094.18	.000464– .0147
U	4244.372	0.0215 – 0.464
	3270.124	.0316 – 1.00
	2865.679	.0681 – 1.00
V	3102.299	0.000147– 0.0100
	3183.406	.000147– .0215
	3134.931	.00147 – .100
W	4008.753	0.00100 – 0.0681
	2896.446	.00215 – .464
	2946.981	.00464 – .464
Y	3327.875	0.000316– 0.0215
	3195.615	.000316– .0464
Yb	3987.994	0.000068– 0.00147
	3464.370	.000681– .0100
Zn	3345.020	0.00147 – 0.0464
	3345.572	.00100 – .316
Zr	3279.265	0.000316– 0.0681

the usual manner, final tamping of the sample being accomplished with a special tamper (fig. 1).

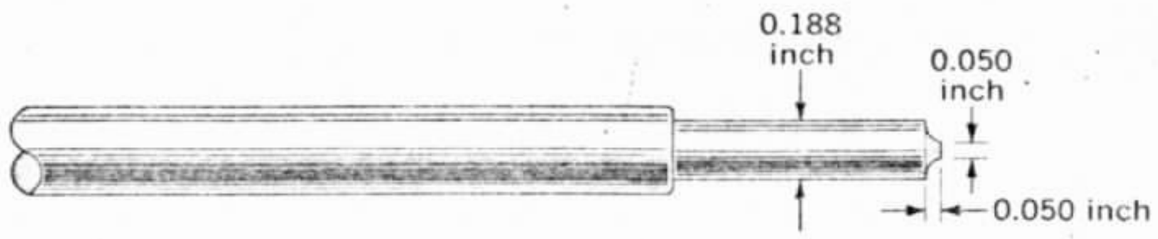

Figure 1.—Aluminum alloy tamper. This tamper provides more surface area than a flat-end tamper and facilitates the escape of gases from the sample with minimum sample loss.

Special efforts are made to assure identical conditions in the arcing of all samples and standards. The jaws in the arc stand were modified by the addition of a simple stop to permit each electrode to be grasped at the same point and cooled to the same extent during each burn.

Because the electrodes are being consumed more rapidly in the gas flow than in air, they require more frequent adjustment to maintain the arc gap. Some sample types form beads during the latter part of the arcing. The size of the bead is a function not only of the composition of the sample but of its mixing with the graphite; the better the mixing, the smaller the bead. Loss of a bead can cause low results for some of the major elements (Si, Al, Fe, and Ca). By controlling mixing and burning conditions for samples and standards, however, the results for these elements usually fall within the precision and accuracy of the method.

Each spectrum contains two cadmium reference lines superimposed with a lamp and mask assembly as described by Helz (1973), who also described the photoprocessing equipment for the 508-mm plates and the densitometer-recorder system.

Plate calibration, line finding, construction of analytical curves, and calculations are performed by the computer and will be described in detail in a subsequent paper by Walthall (1973).

RESULTS AND DISCUSSION

Detection limits and useful concentration ranges for individual lines of 68 elements determined with this technique are given in table 1. These limits and ranges are a function of the analytical lines chosen, exposure, interferences, and limitations of the recording system. A third significant figure is used solely for programing convenience. Of the 206 lines, 27 occur in the cyanogen band region and include the most sensitive lines for Ce, Cr, Eu, Gd, K, Mo, Pr, Rb, Sc, Sr, Th, Tl, W, and Yb. The detection limits for most elements are equal to or better than those obtained by the visual semiquantitative method. We are programing the computer for correcting interferences; many of the limits and ranges will be changed as a result.

A detailed study of the precision of this method, using a variety of sample types, has been made in a study of twelve U.S. Geological Survey standard rocks by F. G. Walthall, A. F. Dorrzapf Jr., and F. J. Flanagan (unpub. data). The precision is within the range of +50 to −30 percent of the amount present, as expected of a semiquantitative method, and approaches ±10–15 percent for many elements, as normally expected of a quantitative method. Data on standard diabase W-1 from this study are given in table 2.

Table 2.—*Standard deviation and coefficient of variation for standard diabase W-1*

[From F. G. Walthall, A. F. Dorrzapf, Jr., and F. J. Flanagan, unpub. data]

Element	Average concentration[1]	Standard deviation[2]	Coefficient of variation[3]
	Percent		
Si	27.7	2.3	8.30
Al	9.77	1.2	12.3
Fe	9.29	.20	2.15
Mg	6.13	.15	2.45
Ca	8.67	.45	5.19
K	.652	.096	14.7
Ti	.727	.048	6.60
Mn	.186	.006	3.23
	Parts per million		
Ba	141	9.7	6.88
Co	53.1	2.7	5.08
Cr	157	6.7	4.27
Ga	21.2	1.2	5.66
La	17.8	2.1	11.8
Nb	7.1	2.5	35.2
Ni	86.4	8.7	10.1
Pb	7.26	.73	10.1
Sr	248	15.6	6.29
Y	26.4	2.3	8.71
Yb	4.23	.24	5.67
Zn	147	4.9	3.33
Zr	142	16.3	11.5

[1] Average of six determinations; three bottles, two portions of each.
[2] Square root of the error mean square calculated in the analyses of variance.
[3] Coefficient of variation equals standard deviation times 100 divided by average concentration.

Despite marked improvements in spectrochemical methods in the last several decades, the determinations of the major constituents of a rock have been generally within the province of chemical methods. In the hope that this computer-based method might yield data for the major constituents that would be comparable to chemical determinations, duplicate portions of 20 samples have been analyzed randomly. These samples had been previously analyzed chemically.

To determine if the differences between the chemical and spectrographic data were significant, the t test in the form $t = \frac{\bar{d}\sqrt{n}}{s_d}$ as shown by Youden (1951, p. 28) was used. In the summary shown in table 3, the chemical data were assumed to be correct, and the differences—chemical minus spectrographic—were converted to percent of the chemical data. The average difference, $\bar{d}$, and the standard deviation of the

Table 3.—*Comparison of chemical and spectrographic data for 20 samples*

[$\bar{d}$ is the average difference in percent from chemical data, n is number of pairs, t is the t distribution with $n-1$ degrees of freedom. A positive difference indicates that values of chemical data are greater. NS indicates that the average difference is not significant at $t_{0.95}$]

Oxide	Range of oxide from chemical data (percent)	$\bar{d}$	n	t	
				Calculated	From tables
SiO_2	45.1 –76.4	+11.3	20	3.89	2.09
Al_2O_3	10.9 –22.6	+19.8	20	3.95	2.09
Fe_2O_3	1.46–16.8	+1.82	20	.812 NS	2.09
MgO	.06–13.2	+16.1	20	2.35	2.09
CaO	.34–12.7	–2.92	20	.434 NS	2.09
K_2O	.09– 6.23	+2.19	16	.460 NS	2.13
TiO_2	.09– 2.67	+24.2	20	3.83	2.09
P_2O_5	.01– .99	–16.3	10	1.89 NS	2.26
MnO	.03– .24	–11.8	20	2.79	2.09

differences, s_d, were calculated from these n differences. The tests showed that the paired differences for Fe_2O_3, CaO, K_2O, and P_2O_5 were not significant and both methods may be said to yield comparable data. Further refinements are necessary for the determination of the remaining oxides but especially for SiO_2, Al_2O_3, and TiO_2, for which the differences are significant at greater than $t_{0.99}$.

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SPECTROCHEMICAL COMPUTER ANALYSIS—INSTRUMENTATION

By A. W. HELZ, Washington, D.C.

Abstract.—A microphotometer is described for making magnetic tape recordings of spectra 480 mm long from 102- by 508-mm photographic plates. Transmission readings are recorded at a rate exceeding 1,300 per second for every 5.08 μm of length of the spectrum: A two-line cadmium fiducial line system and a developing tank for 102- by 508-mm plates also are described as equipment ancillary to a system of computer spectral analysis applied to the spectrochemical analysis of geologic materials.

The recording-computer system for a complete spectrochemical analytical procedure that was previously outlined (Helz and others, 1969) is now in routine service. Computer-prepared analytical reports show concentrations of 69 elements determined from a single 70-second microphotometric scan of a spectrum between 2,300 and 4,700 A. A search is made by the computer for about 400 spectral lines from among 92,000 optical transmission readings. All the calculations are completed automatically, including conversion of transmissions to intensities, background correction, reference to analytical curve data for concentration determination, spectral interference allowance, and choice of the "best" value on the basis of a set of line-intensity rules. Among the many changes that the procedure has undergone during the last few years are the use of 102- by 508-mm (4- by 20-inch) plates, studies of many new analytical lines, and a complete change in the line-finding logic with the attendant two-cadmium-line principle. These changes have resulted from the cooperative efforts of several of my colleagues.

Automatic trace-element analysis of geologic materials was one of the goals of this program. It was anticipated that the most refined principles of metrology would be involved because of (1) the unusually high complexity of spectra for silicate rocks and (2) the very high accuracy requirements for finding very weak lines at a predetermined wavelength (as opposed to the converse of identifying by wavelength a readily apparent line). With the objective achieved it was obvious that advantage could be taken of this system in developing many new applications.

This report describes a microphotometer designed to meet the requirements of accuracy and speed. To be effective, the microphotometer recording system had to be capable of recording a spectrum nearly 500 mm long at constant velocity from start to finish in no more than 90 seconds, making at least 1,000 transmission readings per second. Transmission readings at 5-μm intervals along the spectrum, based on known positions within the spectrum, were also required.

Acknowledgments.—C. J. Massoni not only did all the on-the-job shop work referred to in this report, but also designed a large number of mechanical refinements. Walthall (1973) devised, completed, and tested the complex computer programs in use. His work dealt with line-finding problems, line-peak definition, plate calibration, curve fitting, background treatment, element concentration calculations, report formatting, and many other details. Dorrzapf (1973) worked out details of the applied spectrochemical procedure, particularly those of the argon-oxygen shielded arc and of plate exposure and processing.

The author is particularly appreciative of help provided by A. E. Johnson and Vilmars Fimbers, of the Moore Special Tool Co., for making possible the modifications in their standard measuring machine.

RECORDING SYSTEM

The complete recording system is shown in figure 1; it includes the tape recorder, the relay rack containing most of the electronic circuits, and the microphotometer.

The recording of a single spectrum consists of first entering on the tape a 12-digit number for identification purposes. This number is determined by adjusting thumb wheel switches. Second, the memory is cleared, and third, the motor drive for the table is started. The plate containing the spectrum is moved by the motor through the scanning beam at a steady speed. A phototube constantly monitors the scanning beam, which changes in intensity as it is intercepted by the spectral lines. The photoelectric output is sampled for every 5.08 μm of travel of the spectrum plate. The reading is digitized and then stored in the memory bank. The sampling of the photoelectric output is averaged over a short but finite fraction of time between two readings in order to smooth out electronic noise fluctuations. Whenever a predetermined number of readings has accumulated in the memory bank, the entire group of readings is transferred to the tape as a single record without interruption of the constant flow of incoming

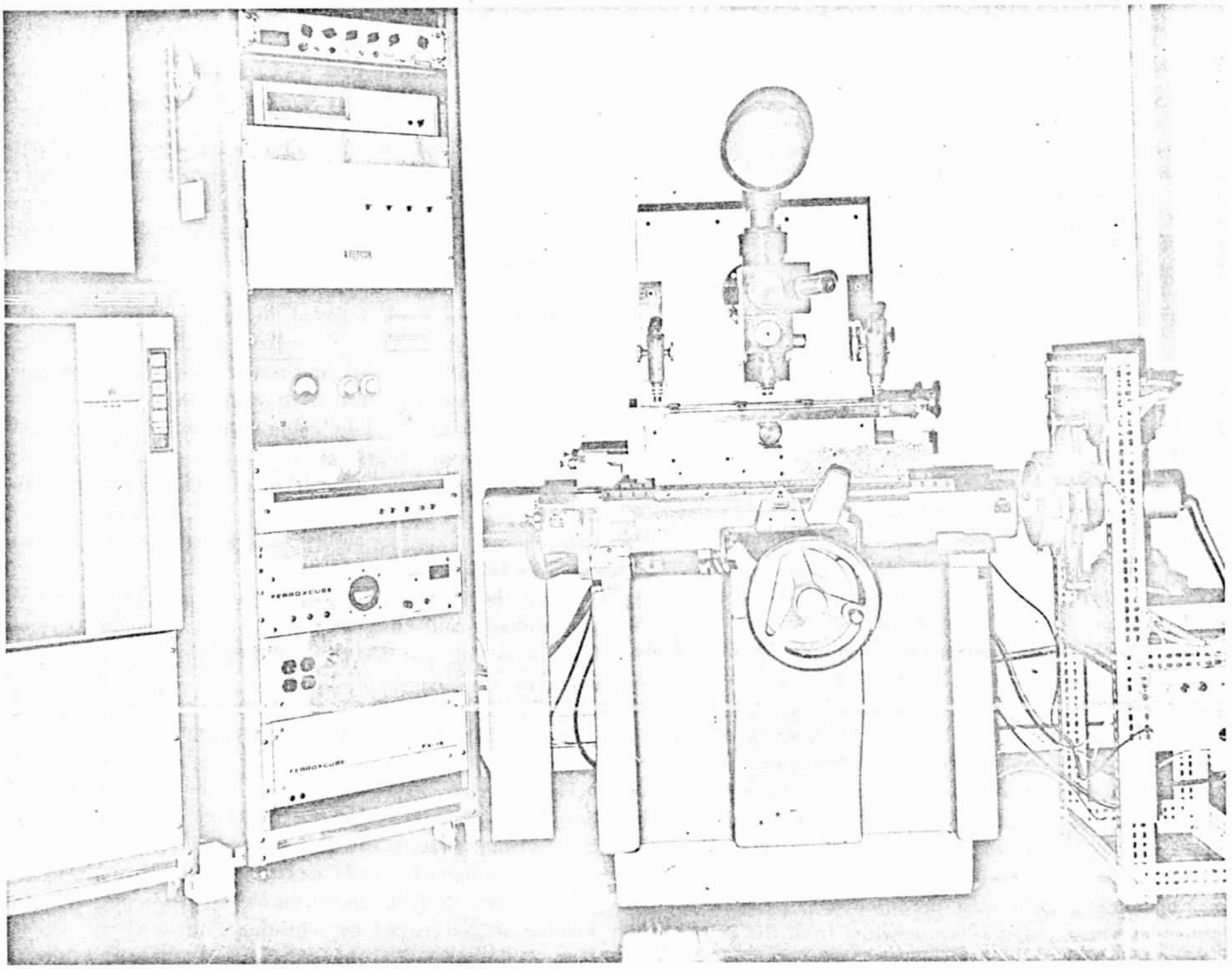


Figure 1.—Recording system. At the extreme left is the tape recorder. The tall relay rack to its right houses power supplies, counter, time devices, a-d converter, memory unit, fixed data entry, numerous control switches, and scanning lamp and phototube adjustment facilities. The microphotometer is in the center, and the power drive for the table is at the extreme right. The microphotometer is about 5½ feet tall.

readings. The tape recorder has the circuitry necessary to produce the computer-required spaces between the records. A limit switch for the table motion and a stop on the control relay rack are activated at the end of a spectrum scan.

The activated stop switch permits the one remaining incomplete record to be recorded and also produces an end-of-file mark on the tape. Thus, all the records for a single spectrum, including an identifier, are grouped into a "file." Vital to this recording process is the condition that no readings be lost. Readings made while a record is being "dumped" on tape and a gap is being formed are kept in proper order in the memory bank. The ordinal number of a reading multiplied by the reading interval determines the basic relationship between length and wavelength. The elimination of the necessity of recording explicit "length" or position data reduces the amount of recorded data by a factor of three. This saving is made possible with the use of a memory bank of sufficient storage capacity to include all the readings of one record plus the number of readings taken during the time required for the complete dumping process.

MICROPHOTOMETER

The horizontal motion of the microphotometer is provided by the Moore No. 3 Measuring Machine.[1] This machine was obtained with a simple vertical bracket in place of the standard vertical column (fig. 2). The machine was also supplied with a modification of the longitudinal traverse to provide for 483

[1] Moore Special Tool Co., Bridgeport, Conn.

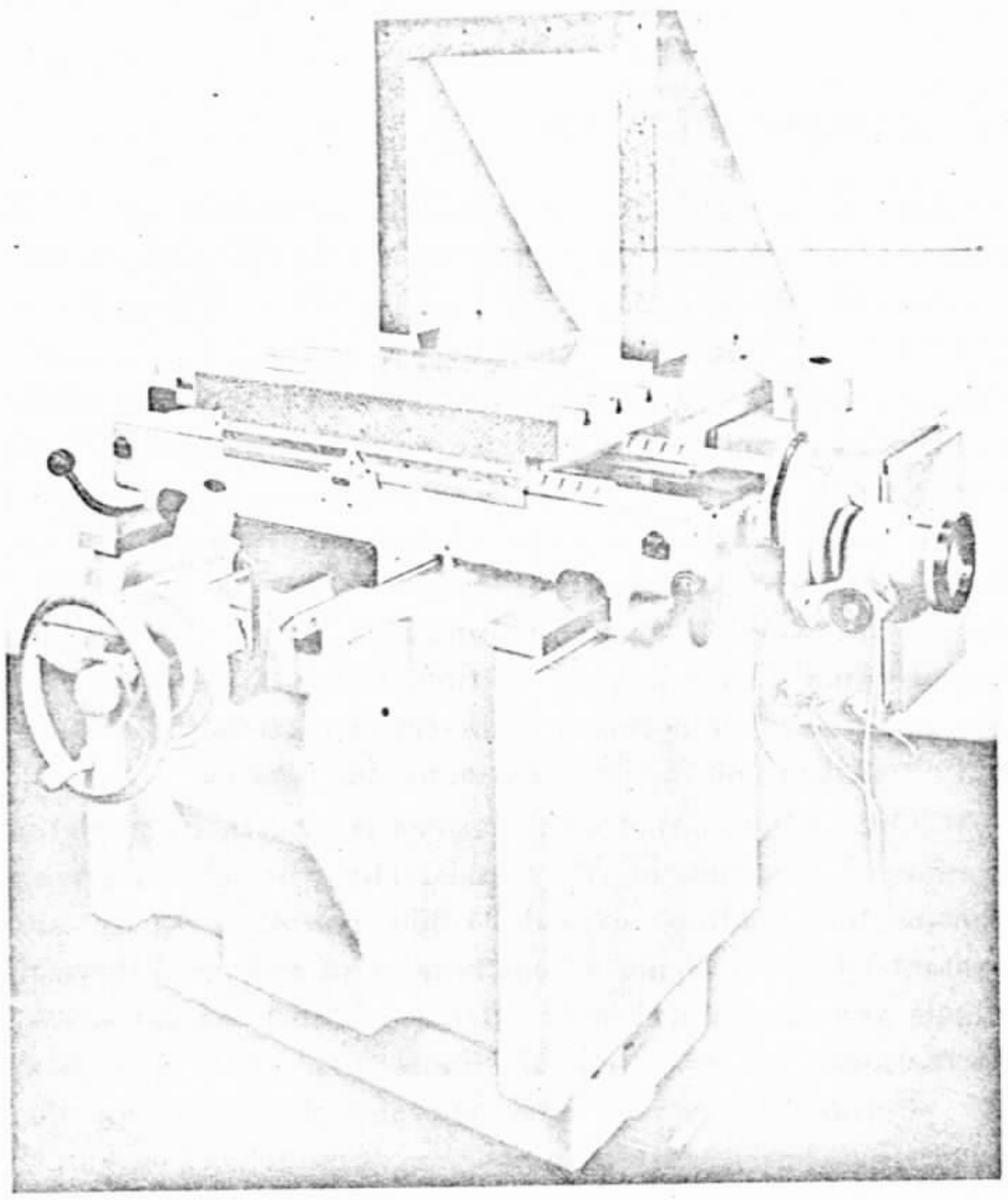


Figure 2.—Measuring machine with bracket for installing the microphotometer optics. Height is about 5 feet.

mm rather than the standard 458 mm of travel. Although this change was made at the risk of some loss of ruggedness, it was not considered serious because of the light-duty application. Concern over the comparatively high speed requirement determined our selection of roller-bearing support, on advice of the manufacturer, for the table's longitudinal motion. The heart of this machine and the fundamental length determinant of the spectral reading system is the 533-mm-long lead screw having tolerances of +0 and −0.9 μm overall and 0.4 μm in any 25-mm section (+0 and −35 millionths of an inch overall and within 15 millionths of an inch in any 1-inch section). The optical system is mounted on a 559- by 508- by 19-mm aluminum-alloy plate bolted to the vertical bracket of the measuring machine. A spectral plate holding-and-orienting device, cut from a single piece of normalized mild steel 610 by 152 by 38 mm, is mounted on the table of the measuring machine (fig. 4A). This plateholder is supported at the ends, 48 mm above the table, to provide the space needed for the light path below the spectral plate. A bidirectional, incremental, rotary encoder is mounted with its axis in line with the longitudinal screw and is connected to the screw with a precision bellows coupling.

The optical system follows conventional practice for good resolution, high contrast, and low scattered or diffuse light detection. The optical system is not entirely in one plane as seemingly indicated in figure 3. For the source area and for the end with the phototube the plane of the drawing is horizontal; the remainder of the drawing is in a vertical plane.

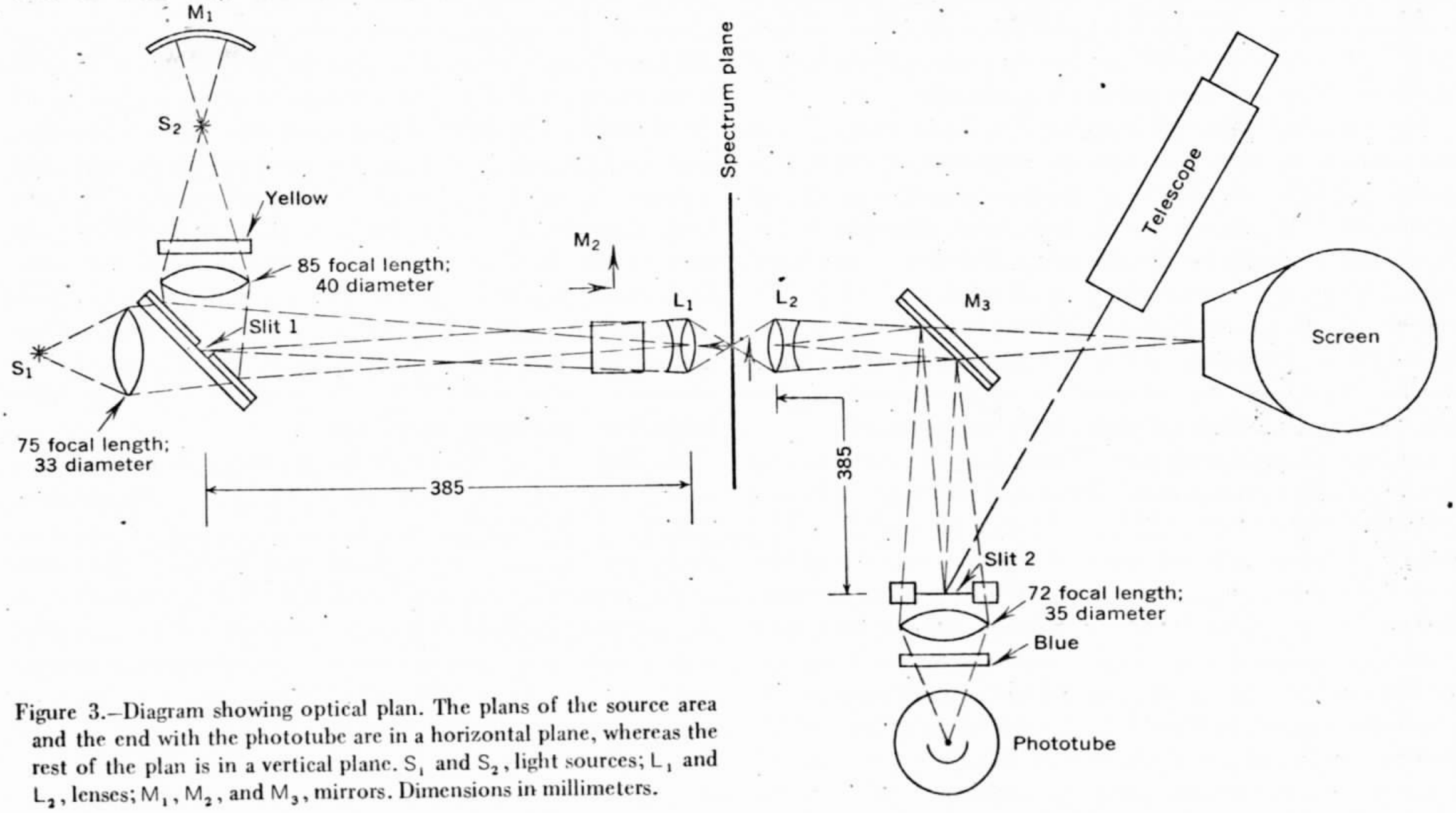


Figure 3.—Diagram showing optical plan. The plans of the source area and the end with the phototube are in a horizontal plane, whereas the rest of the plan is in a vertical plane. S_1 and S_2, light sources; L_1 and L_2, lenses; M_1, M_2, and M_3, mirrors. Dimensions in millimeters.

Two low-power light sources are used. The reading source, S_1, is d-c powered and illuminates entrance slit 1 (fig. 3). The source S_2 is a-c powered and illuminates the front mirror surface of the entrance slit. This source provides field illumination for the viewing screen. Both lamps are 6-volt, 3-amp, microscope illuminator type. The fixed entrance slit consists of a precision-ruled, 100-μm-wide window in a mirror. A 32-mm-focal-length Micro-Tessar lens, L_1, focuses an image one-tenth the slit size on the plane of the spectrum. This image for the scanning light, about 7 μm wide, was selected to be about one-quarter of the width (a sizable fraction) of a spectral line and about 1 mm in length, which is as long as practical. Precision adjustments of slit 1 for translation and rotation are provided for alinement relative to the spectral lines and slit 2. The box holding the source section of the microphotometer is shown in figure 5.

The "observer" half of the optical system starts with a 32-mm Micro-Tessar lens, L_2 in figure 3, having specifications identical with those for L_1. A blue image of the spectral area (which is illuminated through slit 1) is formed by L_2 on a second slit (slit 2) via a dichroic mirror, M_3. The yellow field illumination of the same spectral area is transmitted through the dichroic mirror to form a viewing image on the screen. Magnification of the spectrum is about 10 times at the exit slit, and 100 times at the screen. An image of slit 1 is also visible on the screen. Slit 2 has width and height adjustments and is accurately rotatable for alinement. A blue filter in front of the phototube aids in the further elimination of the light of the field illuminator source from the phototube.

The telescope indicated in figure 3 is used to set up a run but cannot be used for accurate alinement because it is positioned off axis. This was done to permit viewing past mirror M_3. Initial alinement and focal adjustments are facilitated by replacing the phototube-filter-lens combination with a low-power microscope focused on the rear of the slit. Focus, orientation, and position of the two slits and spectral lines may be accurately adjusted in this manner. Once this is accomplished and the viewing screen is adjusted, routine alinement may be made precisely on the viewing screen.

Location of the optical parts discussed above is illustrated in figure 4. The photopickup illustrated in figure 5*A* is a commercial phototube and a solid-state preamplifier. This combination has sufficient speed of response and is preferred over a multiplier phototube when the light level is adequate, because of its greater long-term stability and freedom from drift. The outboard microscopes, shown in figures 1 and 4*A*, are used to aline the spectra parallel to the table motion. The plateholder, visible in figures 4*A* and *B* with a spectral plate in position, has a rotational adjustment about a vertical axis for achieving this parallelism. The plate-supporting surface of the plateholder was machined and hand scraped to be parallel to the table, within 2.5 μm, throughout its entire motion.

A variable-speed d-c motor and a gear reduction drive were used at first for the scanning motion. However, spurious spectral lines occasionally were observed when scanning at the maximum speed, and these were traced to vibration of the vertical optical train caused by the gear drive. Although the problem was eliminated by changing the power drive, strengthening of the brackets of the optical column is recommended. The revised power drive now in use, with the worm and helical gears replaced by a 165-mm-diameter pulley, is shown in figure 6. This pulley is driven with two reversible, constant-speed, a-c motors mounted diametrically opposite the screw shaft. These motors are wired in parallel. A Buna-N O-ring, 240 mm in diameter and 7 mm in cross section, transmits the power of this dual motor arrangement with very little stress (other than that of rotation) on the precision screw and bearing.

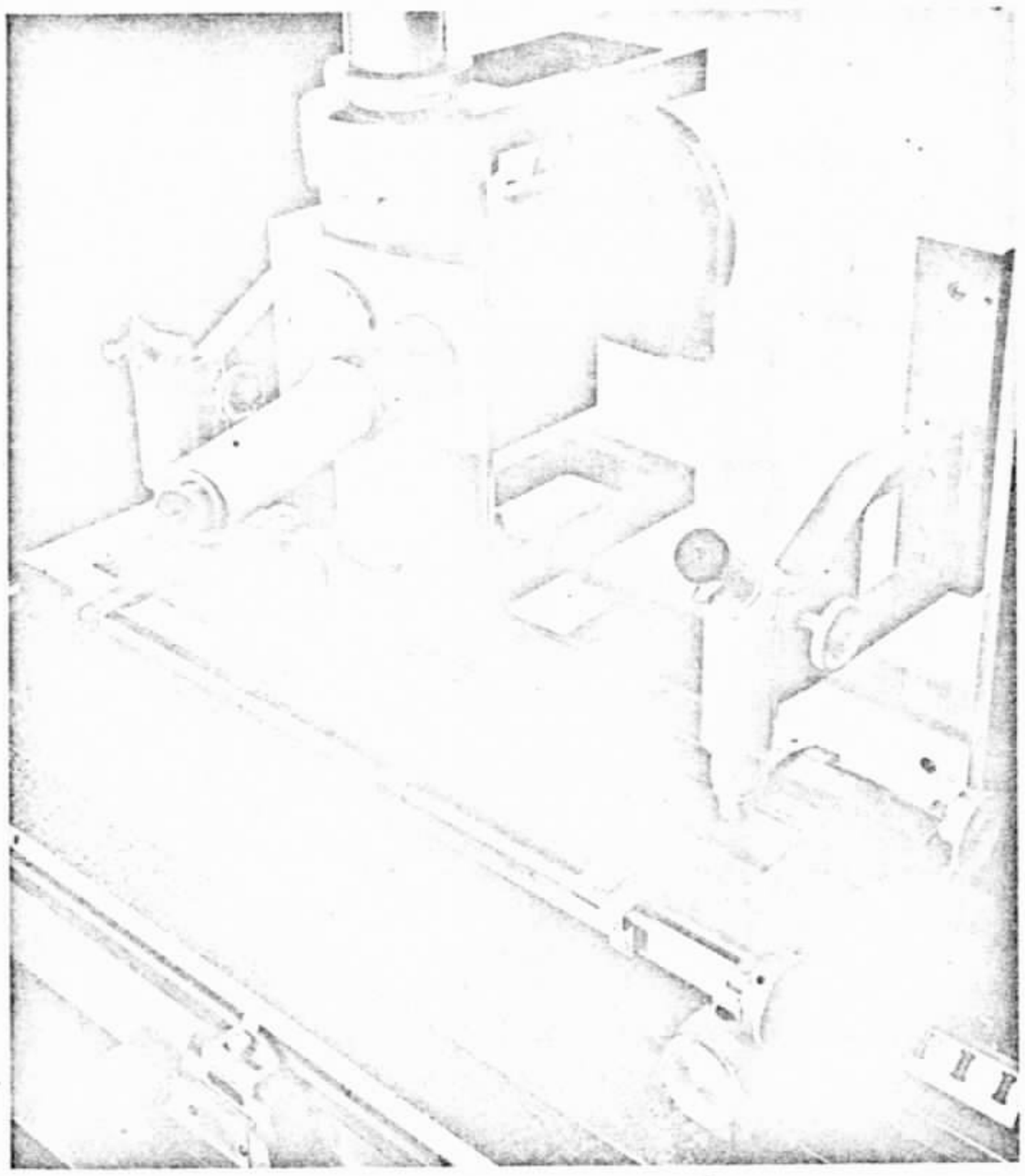
At this writing, a motor-drive speed is used that completes scanning a spectrum in 70 seconds. Thus the rate of taking transmission readings exceeds 1,300 per second. We are hesitant to go to higher speeds because of unknown thermal effects and mechanical wear effects on the precision screw. Furthermore, we are close to the limits of speed of response of the photometric system used and also limitations of the particular recording system in use.

FIDUCIAL LINES

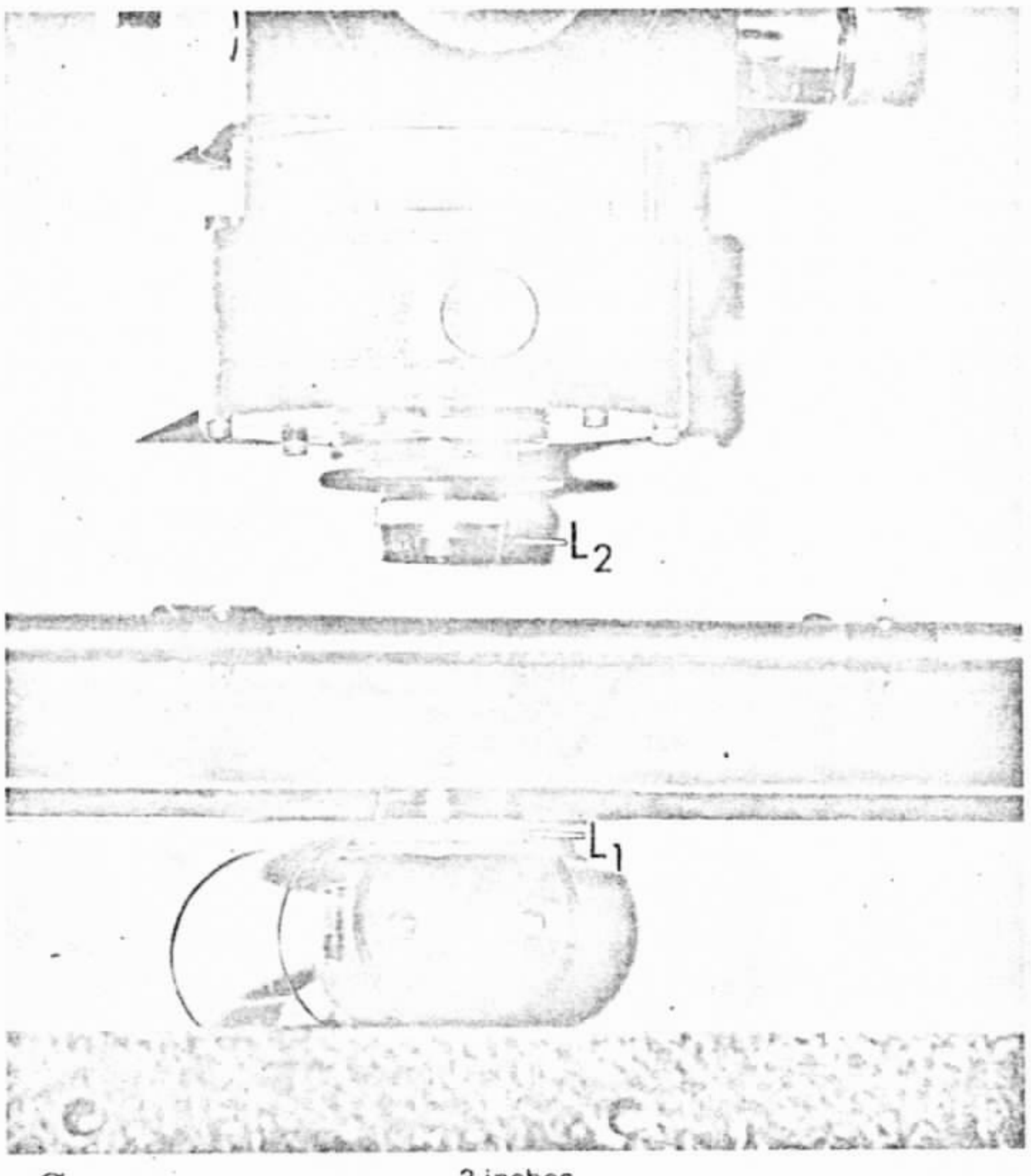
Computer line finding in our earlier work depended upon having Cd 2288.02 A and numerous iron lines in each spectrum. The cadmium line was obtained with an Osram-type discharge lamp and selective filtering, and the others resulted from having iron at a concentration of at least 1 percent in each sample. The latter requirement represented a nuisance value and limited the determinations of iron in the analytical scheme. As work progressed, it became apparent that the reading-number differences between given lines, even from the first to last lines in a spectrum, tended to be the same. Differences that did exist showed a definite pattern rather than random scatter, suggesting that the precision of the system, including the spacing of the microphotometer measurements, was of such a high order as to make the many-iron-fiducial-line procedure superfluous.

The differences in the length of a spectrum referred to above may be thought of as a "stretching" error. Temperature changes of either the spectrograph or the microphotometer, or both, could produce errors of this kind. However, the source of this stretching error was found to be mainly mechanical, in the spectrograph, arising from a failure of the photographic plate to slide in a fixed plane as it is racked from spectrum to spectrum. Adjustment of the plateholder reduced this problem to a tolerable level. The residual mechanical error and the plate-to-plate temperature errors are effectively diminished by the use of two cadmium fiducial lines as described below.

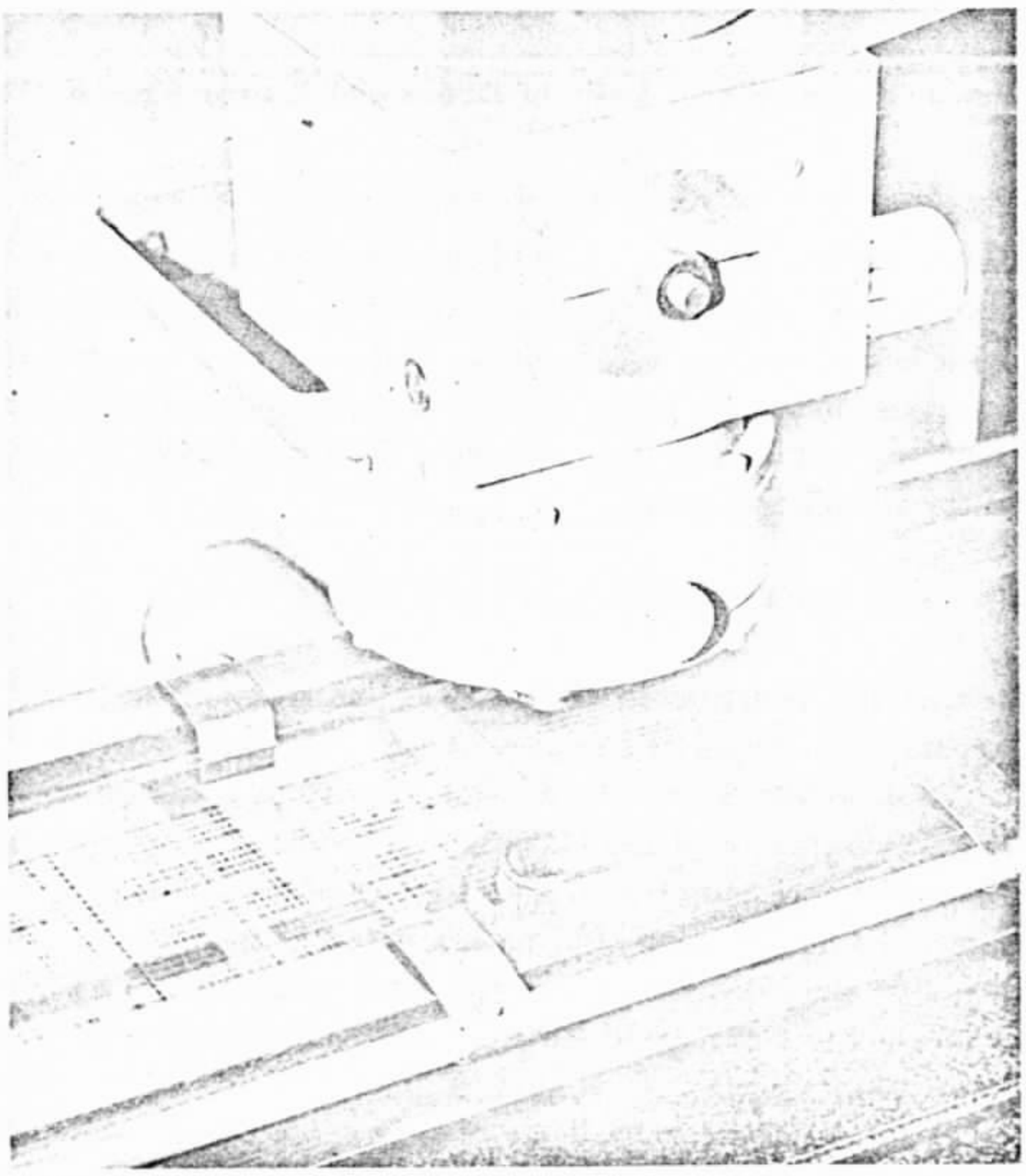
Cadmium fiducial lines are recorded in each spectrum with the use of a 19-mm-diameter cylindrical mask mounted as close as possible to the focal plane of the spectrograph. As diagramed in figure 7, there are three positions. When set in



A

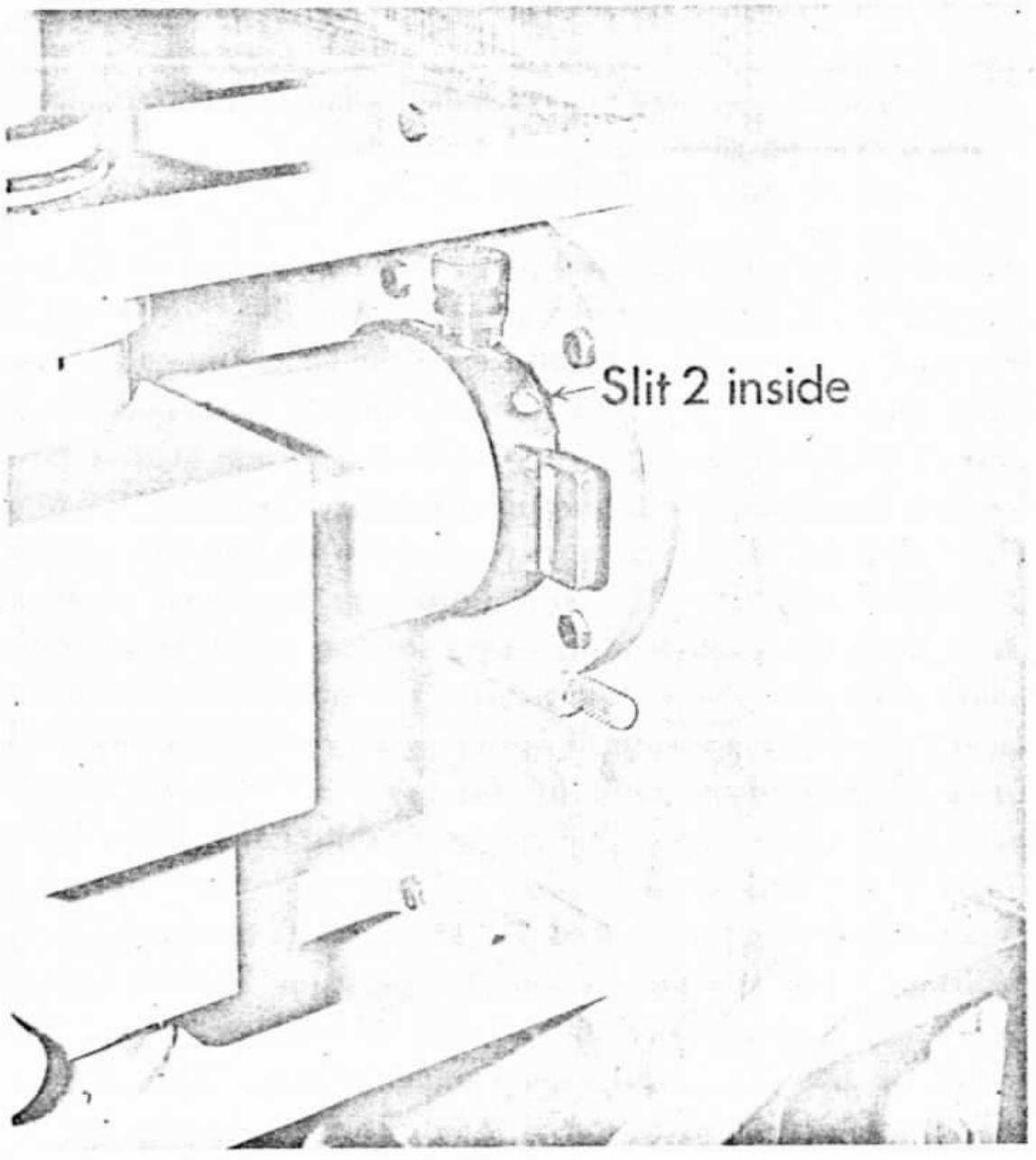


C



B

2 inches



D

2 inches

Figure 4.—Front of optical support panel of microphotometer. *A*, With spectrum plate in position. *B*, Closeup view of central part of *A*. *C*, Edge of plateholder and the two Micro-Tessar lenses. *D*, Exit slit.

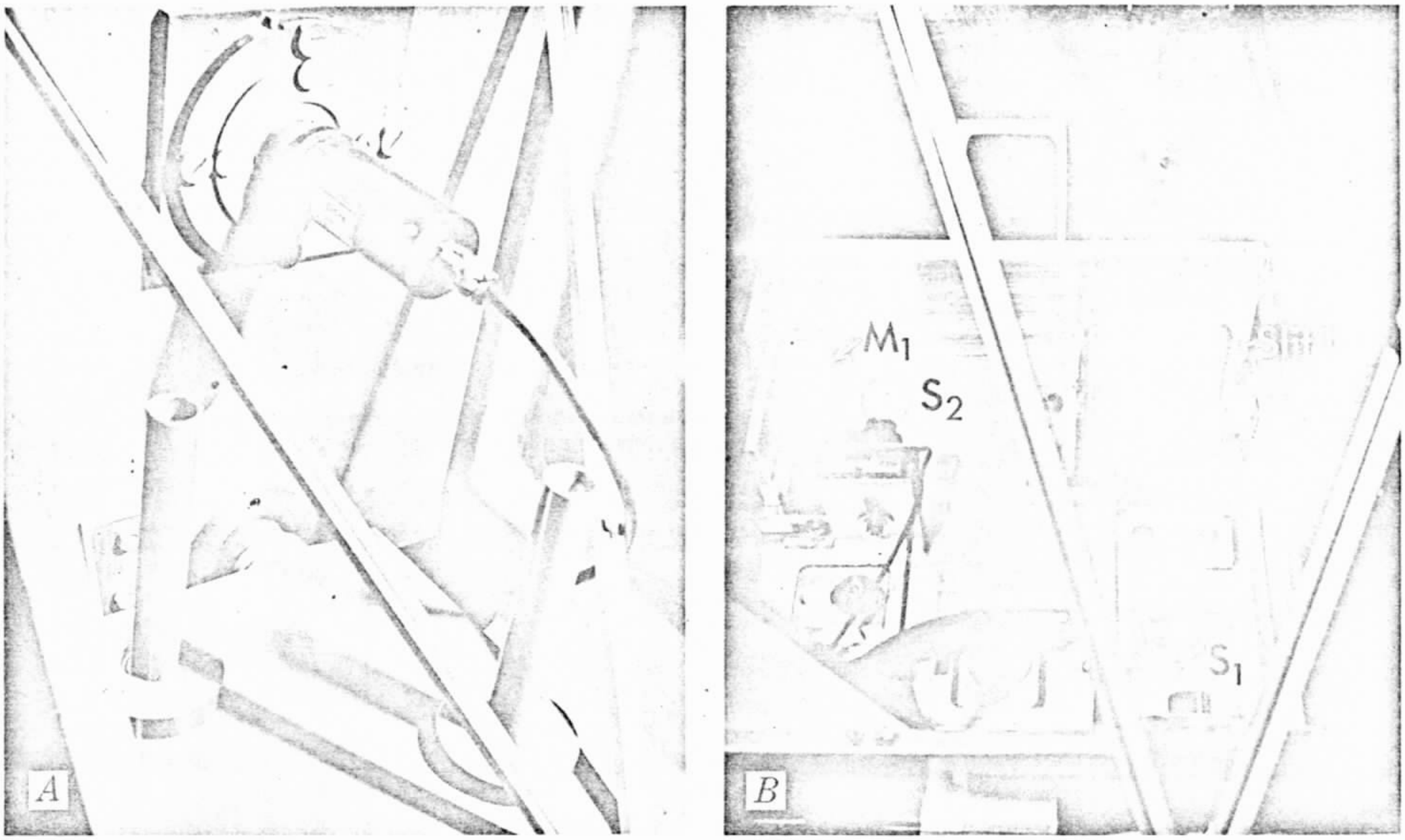


Figure 5.–Rear of optical support panel of microphotometer. *A*, The photopickup (4¼ inches long) is at the top center. The light-source section, at the bottom, is covered and has chimneys directly over the lamps for convection ventilation. *B*, A view of the box with its cover removed. The box is 10 inches square.

position 1 the entire spectral range may be exposed except for two 4-mm-wide spectral ranges, each about 20 A. Position 2 of the mask excludes from exposure all the spectrum except the same two narrow ranges. Position 3 differs from position 1 only in height of the openings. Position 1, 4 mm high, is used for iron two-step plate-calibration exposures; position 3, 2 mm high, is used for sample exposures. With this device Cd 2748.58-A and Cd 4415.70-A lines may be placed in small clear areas in each sample spectrum in exact wavelength relation to the sample lines. After the plateholder has been racked to a new position, it is exposed to cadmium radiation from an Osram-type cadmium lamp for 20 seconds through position 2 of the mask, thus exposing the photographic plate through the two small windows. A solenoid, timer-operated mirror facilitates this procedure. The mask is then rotated to position 3 for exposing a sample spectrum. Special care is taken to eliminate any disturbance of the position of the spectrum and the photographic plate between the cadmium and sample exposures.

The two cadmium lines are clearly identifiable because of the elimination of spectral background in their immediate vicinity; they are easily and uniquely located by the computer. The wide wavelength spread between the two cadmium lines assures precise data for stretching correction in the computer line-finding calculations. Using the two cadmium lines as described above has the additional advantage of maintaining precision, inasmuch as the intensities of the cadmium lines and their spectral background are under control and independent of the sample spectrum.

PHOTOGRAPHIC PLATE PROCESSING

Specially constructed plate processing, washing, and drying apparatus is required because of the 508-mm length of the spectral plates. A developing tank (fig. 8) is made of acrylic plastic sheets except for a stainless steel separator between the developer and stop-bath sections. The photographic plate is lowered into the long thin tank compartments endwise with stainless steel strips (not shown). Small volume of developing solution (450 ml), good stirring, and temperature control are basic requirements. Fixer and stop-bath solutions are circulated through heat exchangers in an external thermostatically controlled bath. The developing solution is in thermal contact with the stop bath by means of the stainless steel separator; temperature uniformity and stirring of the developer is accomplished with a gaseous burst. Nitrogen is introduced at

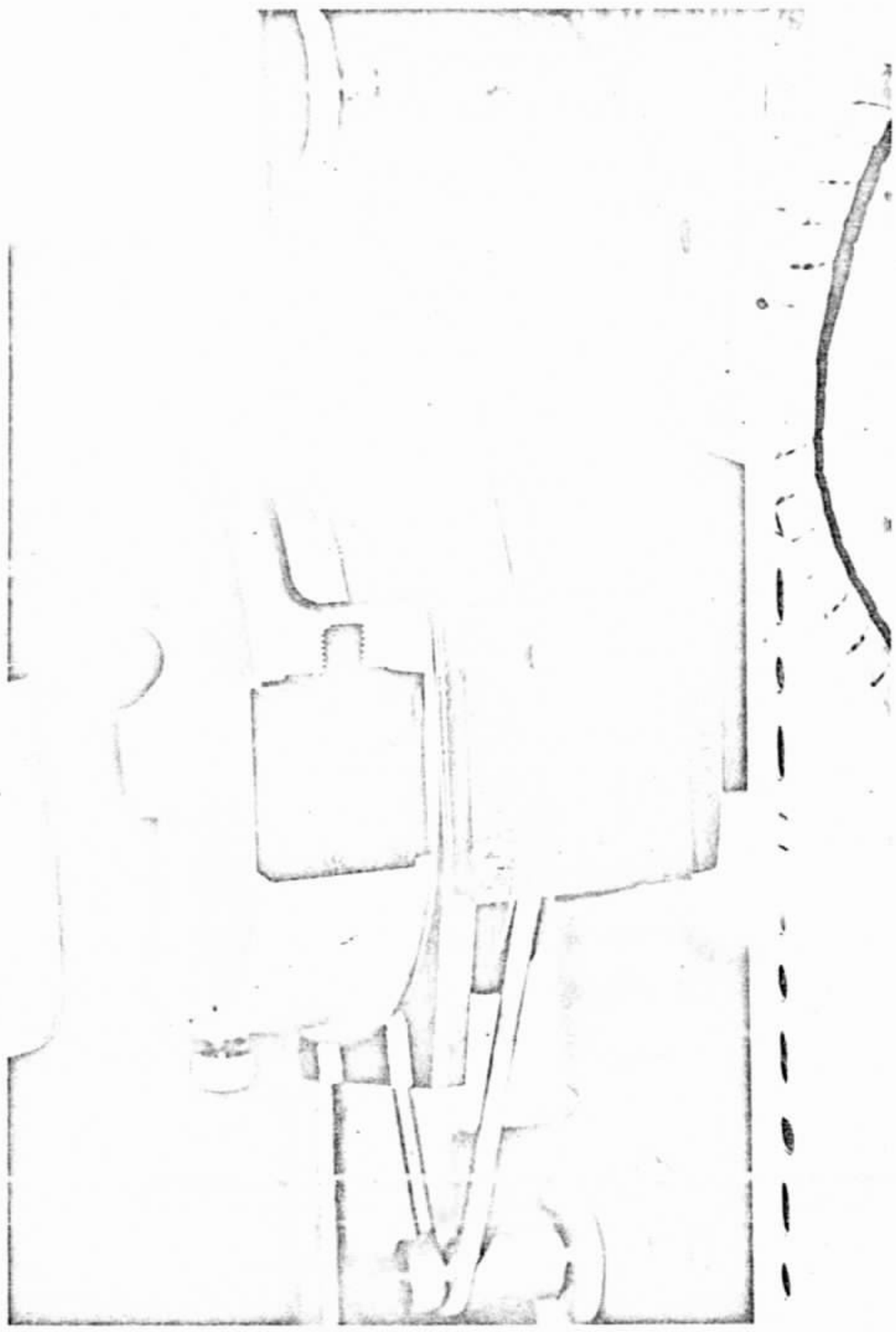


Figure 6.—Motor drive. The two a-c motors are mounted above and below the 165-mm pulley. The diameter of the central cylinder is about 6 inches.

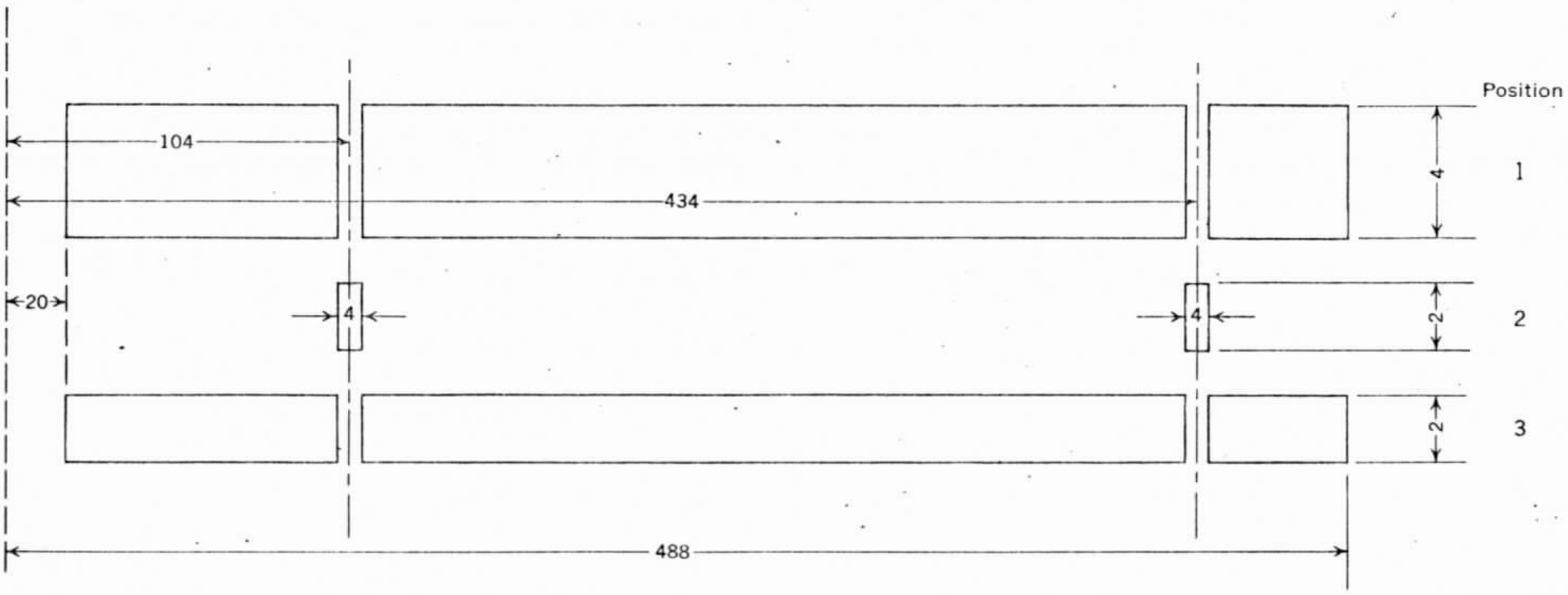


Figure 7.—Diagram showing the plan of the mask mounted on the spectrograph near the focal plane. Not drawn to scale. Dimensions in millimeters are a function of the dispersion of the particular spectrograph employed. See text for explanation.

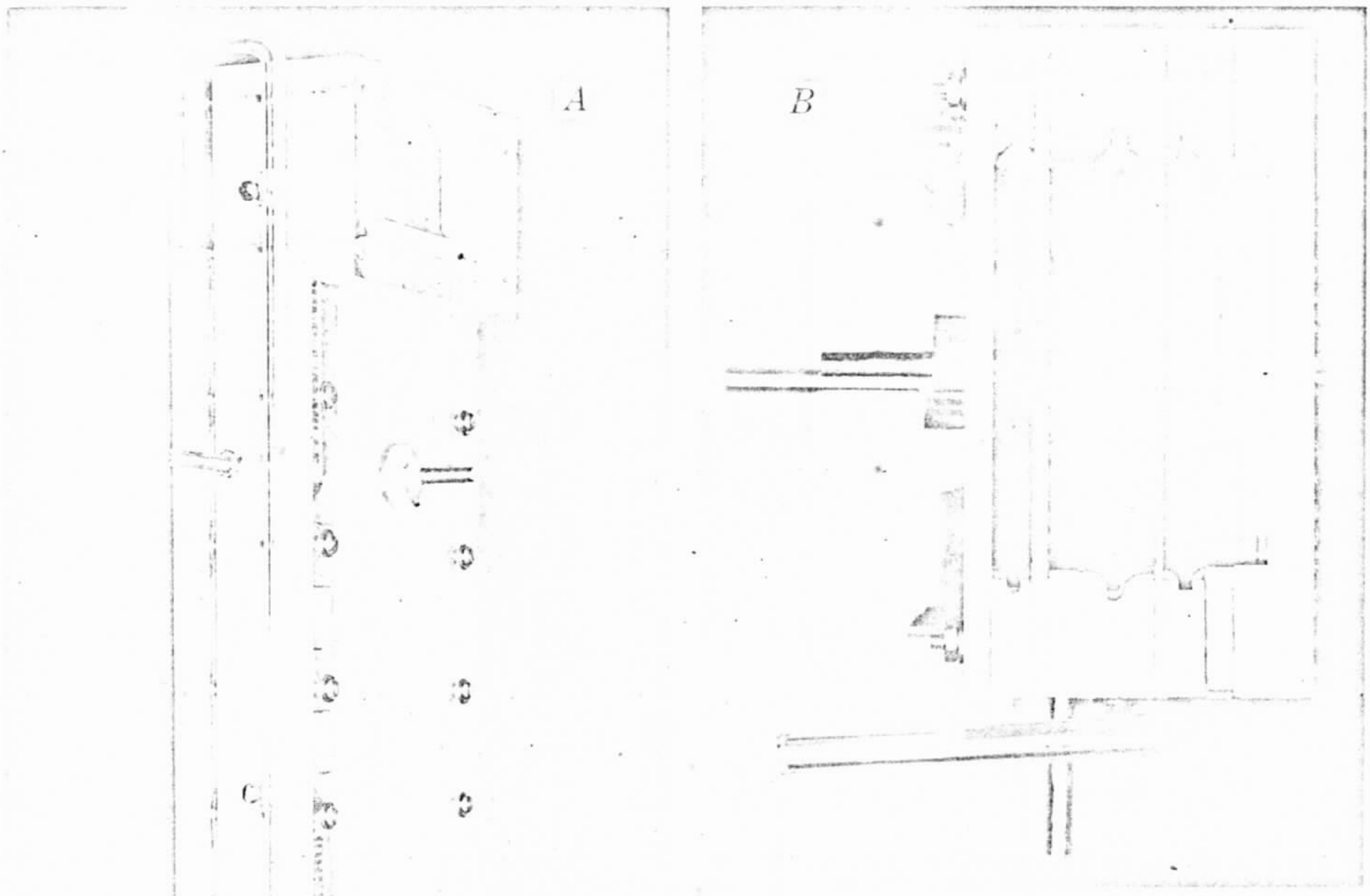


Figure 8.—Developing tank. *A*, Side view, tank is 25 inches tall. *B*, Top view. 1, Developer section; 2, stop bath; and 3, fixer. The longer dimension is 6 inches. Note in *A* and *B* that the developer section is widened near the top to prevent overflow from gaseous burst.

the top level of the tank and flows down the glass tube to the bottom where it is connected to a stainless steel "bubble" tube extending across the bottom of the tank and about 38 mm below the end of the photographic plate. Essential to proper stirring, the gas is allowed to escape to the atmosphere through an alternate vent at a constant carefully adjusted rate with enough impedance in the line to hold the liquid level in the glass tube near the bottom—just short of escaping into the developing solution. This quiet part of the cycle is timed for 8 seconds. A 2-second stirring phase obtains when a solenoid cuts off the escaping gas.

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SPECTROCHEMICAL COMPUTER ANALYSIS—PROGRAM DESCRIPTION

By FRANK G. WALTHALL, Washington, D.C.

Abstract.—The computerized system of spectral analysis performs determinations of 68 elements in geologic materials. The samples are arced under carefully controlled conditions in an argon-oxygen atmosphere and the spectra are exposed on 102- by 508-mm (4- by 20-inch) plates. Transmittance readings taken every 5μm along the spectrum are recorded on magnetic tape, producing more than 90,000 readings in 70 sec. The computer program described examines the data, searches for a maximum of 500 spectral lines, and after treating the results prints concentrations for the elements on a report form. The plates are calibrated every 250 A, transmittances are converted to intensities, backgrounds are subtracted, interferences are recognized, and one final answer is chosen from among several preliminary answers for each element. Concentrations are obtained from analytical curves prepared prior to the sample run. Samples are run under the same carefully controlled conditions that were used to prepare the analytical curves.

A computer program (the final program) has been written to treat transmittance data recorded by the magnetic tape system described by Helz (1973) from plates prepared under the conditions described by Dorrzapf (1973). The program was written in Fortran IV and was designed for execution on a large computer. As the system was to be applied primarily, but not exclusively, to silicate rocks with major emphasis on trace elements, certain procedures were chosen to accommodate the silicates. Additional decisions involved in the design of the total system were influenced by making it no less accurate than the visual semiquantitative spectrographic analysis method in use in Geological Survey laboratories (Myers and others, 1961). The visual method compares previously prepared standard plates with freshly prepared plates of sample spectra. The choice of a 5-μm interval between readings was based on the minimum number of readings required to suitably define a spectral line on our plates while keeping the total number of readings within reasonable bounds. This factor coupled with rapid-scanning capabilities effectively minimizes the recording time and the quantity of data. One reading covering half the length of a spectral line is taken every 5 μm with about 50-percent overlap of successive readings. This number of readings is ample for finding line intensities. A dependable high-speed tape-recording system obviously is necessary to take full advantage of the potential being offered. The instrumentation described by Helz (1973) measures, digitizes, and records over 90,000 three-digit readings in 70 seconds.

The original concept (Helz, 1965) of the computerized emission spectrographic analysis (ESA) system was to have only one computer program which would perform the complete job from two 4- by 10-inch plates covering the desired spectral range. The first program was written in this form and was applied to the low-wavelength half of the spectrum. It started with the taped transmittance data of the split-filter two-step iron spectrum used for plate emulsion calibration curves (PECC), followed by all the standards spectra for the element concentration calibration curves (ECCC) if any, and ended with sample spectra which resulted in a report listing the concentration of elements present in each sample. Analytical lines were found by this program using many fiducial lines which were provided by a minimum of 1 percent iron in the arced sample. The first program was useful to the cyanogen-band region (about 3500 A). To extend its range to 4750 A for additional lines would have required two plates, larger data-storage facilities for the intermediate results, another wavelength table, and a second computer run for the second plate.

A major reexamination of the problem was undertaken and from this came several important improvements. Use of an argon-oxygen arcing atmosphere clears the cyanogen-band region reasonably well, thus making many additional analytical lines available and aids considerably in obtaining a set of constant conditions by helping to control temperature of burning. The adoption of the single plate, 102 by 508 mm (4 by 20 in.), doubles the wavelength range available for a single recording and permits a single computer run for the entire range.

The computer method had been well proven by this time (Helz, and others, 1969) and the reliability of the entire tape-recording system also had been demonstrated. The accuracy of the scanning instrumentation exceeded expectations and was extremely dependable. These factors suggested an entirely new approach to the line-finding procedure. This much more efficient method became a reality at the same time that additional facilities were installed for superimposing the Cd 2748.58 and Cd 4415.70 lines on each spectrum. Means of providing the two-cadmium-line method are discussed by Helz (1973), and its application is described in the section "Line Finding."

The following preliminary preparations are required for the

final program. Once determined, they need only be monitored periodically as long as spectrographic conditions remain unchanged.

1. Wavelengths of iron lines used for plate emulsion calibration need to be selected and their estimated positions determined.
2. Wavelengths of as many as 500 analytical lines need to be selected and their estimated positions determined. The lines are further identified by priority number, atomic number, and element symbol.
3. Coefficients for an analytical curve corresponding to each of the analytical lines are determined, upper and lower concentration limits selected, and a priority number assigned to all the lines of each element. The curve fitting used for all curves is the polynomial regression method consisting of several subroutines from the IBM system/360 scientific subroutine package (version II, H20-0205).
4. The order in which to print answers is selected.

After the preliminary preparations have been completed, a routine run requires only one data card which is described in table 1. Columns 1–14 are ignored when samples from another job request are being run, but columns 15–80 must be completed.

The spectra are prepared in such a way that good reproducibility is realized. The exposure and development conditions described by Dorrzapf (1973) assure the basic requirements of constancy of plate preparation. These constant conditions are necessary and with some care can reasonably be obtained. Future programing will permit large variations in conditions. For example, minimal interference corrections are now being made during routine runs; however, many such corrections ultimately will be available. As they are completed and added, more lines will produce acceptable answers, and an averaging concept will be used to provide the final answer.

Future plans include the application of this computerized system to rocks and minerals in general. The only rock type allowed to influence basic decisions was silicate rock, which can produce a very complex spectrum. Indications are that the system will work equally well with rock types other than silicates; however, these still need extensive investigation.

Table 1.–*Format of data card required for computer analysis*

[The use of fields 1–12 is optional. If left blank, default values (in parentheses under Description) are assumed. If any of the default values are to be changed, all 12 fields must be completed. Type: A, alphanumeric; I, integer; U, undefined. NA, not applicable]

Field	Column	Length	Description	Type	Symbolic name
1	1	1	(Blank)	U	NA
2	2	1	Kind of conditions (type of wavelength table) (2).	I	KOC
3	3	1	Type of plate calibration treatment (0).	I	TPCT
4	4	1	Number of interferences (3).	I	NI
5	5	1	(Blank)	U	NA
6	6–7	2	Number of files read from tape (40).	I	NF
7	8	1	Number of samples, weight <15 mg (0).	I	NFAMBF
8	9	1	Number of first lines (3)	I	NFL
9	10	1	Number of last lines (3)	I	NLL
10	11	1	(Blank)	U	NA
11	12–14	3	Number of records read from each file (200).	I	NRR
12	15–16	2	Symbol preceding sample number (W-).	A	NSS
13	17–22	6	Job number	I	JOBNO
14	23–27	5	Number assigned to job by spectrographic laboratory.	I	GROUP
15	28–36	9	Number of report	A	NOREP
16	37–60	24	Name of person(s) requesting analysis.	A	FOR
17	61–80	20	Name of analyst	A	NANA

SYSTEM REQUIREMENTS AND RESTRICTIONS

Instrumentation.–The absolute integrity of the recording system is important because the position within the spectrum is not recorded but is determined by counting the number of readings. If a few readings were lost, the many-fiducial-line method of line finding would have to be used.

Spectroscopy.–The combination of the use of argon-oxygen atmosphere and the single long plate provides a very good way to take full advantage of the high-speed recording and the computer handling of the accumulated data. Many chemical elements produce potentially useful spectral lines in the cyanogen-band region, and better answers in general will be obtained by studying all lines possible. The many checks made on the instrumentation and the special care taken during sample preparation, exposure, and plate development assure comparable results over a long time. This permits the use of a single set of analytical curves for analyzing sample spectra over an extended period of time.

The set of constant conditions also permits the proper use of the unaltered function of the plate emulsion calibration curve. If proper control of conditions should falter, means are available for shifting those curves affected.

Computer.–The programs are written in Fortran IV (G level) for execution on an IBM system/360, Model 65 computer. The following automatic data processing equipment is being used:

Release 20 MVT (plus HASP) operating system.
450,000-byte core storage.
One 2314 disk unit.
Two 9-track tape drives.
One 7-track tape drive.
CalComp plotter.
Card punch.
Card reader.
High-speed line printer.

Program.–The wavelength table of analytical lines consists of lines which are relatively free from interferences. Three routine interference treatments which greatly affect a few

elements are used, but correcting for interferences in general is not required to accomplish the present aims.

The final program, exclusive of compilation time and the determinations of plate emulsion calibration curves, requires an average of less than 1 minute per analysis for about 400 lines. The routine plate emulsion calibration treatment requires about 1 minute.

The report form tabulates results from a maximum of 10 samples on two pages of computer printout. These are reduced to standard page size and copied for distribution and filing.

PRELIMINARY PREPARATIONS

Before the final program is used, the following must be accomplished: (1) all lines used must be identified, (2) the dispersion must be determined as the number of readings per angstrom to calculate estimated positions for all lines, and (3) the coefficients must be determined for all analytical curves, and upper and lower concentration limits and priority number must be assigned. The variable KOC (kind of conditions) read in from a card (table 1) presently indicates the dispersion used to calculate estimated positions for the wavelength table used. The wavelength table provides information for each line as shown in table 2.

Table 2.—*Format of cards for wavelength table*

[Type: A, alphanumeric; I, integer; R, real; U, undefined. ECCC, element concentration calibration curve; NA, not applicable]

Field	Column	Length	Description	Type	Symbolic name
1	1–3	3	Element atomic number	I	EAN
2	4–6	3	Line priority number	I	LP
3	7	1	(Blank)	U	NA
4	8–9	2	Element symbol	A	ELSYM
5	10	1	(Blank)	U	NA
6	11–19	9	Wavelength	R	WL
7	20–27	8	Concentration limit, lower.	R	CONCLL
8	28–36	9	Concentration limit, upper.	R	CONCLU
9	37	1	(Blank)	U	NA
10	38–40	3	Source of ECCC points	A	NR
11	41–46	6	Estimated position	I	EP
12	47	1	(Blank)	U	NA
13	48–58	11	ECCC coefficient for constant term.	R	CQCEL
14	59–69	11	ECCC coefficient for first-degree term.	R	CQ1EL
15	70–80	11	ECCC coefficient for second-degree term.	R	CQ2EL

Five programs perform much of the preliminary work required.

1. The RPA (readings per angstrom) program finds 23 dispersion lines in each step of the split-filter iron spectrum, calculates 22 dispersions as number of readings per angstrom, averages the wavelengths used, and fits these points as a straight-line dispersion curve. Although the dispersion curve is not truly linear, a straight-line fit permits estimation of 50-A distances with acceptable accuracy. Averaging several of these curves produces a curve which can be used as long as conditions remain the same.

2. The VFL (virtual fiducial lines) program finds 219 iron lines (same ones used for plate emulsion calibration curves) and by using the dispersion curve from the RPA program calculates the estimated positions of imaginary lines from wavelengths increasing every 50.0 A, commencing with 2250.0 A. Averaging results from several plates gives positions of the virtual fiducial lines.

3. The CEP (calculate estimated positions) program calculates the estimated positions of all wavelengths read in by using the positions of the virtual fiducial lines, calculated by VFL, with the dispersion curve from RPA.

4. The EPL (estimated position of lines) program performs line finding for all wavelengths read in for analytical lines from recordings of standards spectra. These results are carefully studied because they will considerably influence any decision to adjust the estimated positions or to use them as calculated. Also, these results provide the points which are fitted as element concentration calibration curves.

5. The PS (point selecting) program fits points from the EPL program as second-degree analytical curves, suggests concentration limits, and rates the curves on a 0–10 basis as an aid in assigning priorities. Our first wavelength table consisted of lines which had been used in other spectrographic methods. We are now using about 400 lines which we consider the most useful of the more than 10,000 lines which have been investigated. This PS program is discussed in more detail in the section "Element Concentration Calibration Curves."

The dispersion curve and the positions of the virtual fiducial lines are calculated from five plates and averaged before being used to calculate estimated positions of desired element lines. After the estimated positions have been calculated, they are used by the EPL program to find lines in spectra from standards. The positions where lines are actually found are given considerable weight as a basis for adjusting the calculated estimated positions. These EPL program results from standards provide information for selecting the permanent estimated positions for the wavelength table which will be used for sample spectra. The manual selection of the data from the EPL runs to be fitted by the PS program for element concentration calibration curves provides ample opportunity for a thorough examination of each point which will be fitted. This becomes useful information when finally deciding upon a curve. All the analytical curves to be used for a sample run are selected prior to the sample run. The PS program prepares a tape for use by the CalComp plotter. Both the points and the smoothed curve are plotted (see fig. 4). This visual aspect is most helpful in making many decisions about a curve—for example, setting the concentration limits and assigning priorities.

FINAL PROGRAM

During a routine analysis by the final program the following occurs:

The plate emulsion is calibrated 10 times, once each 250 A between 2250 and 4750 A, thus determining 10 plate emulsion calibration curves.

Line finding is performed and followed by an evaluation of the results.

Preliminary answers are calculated where possible by using the appropriate coefficients of an element concentration calibration curve and, if not possible, a code is assigned.

Temporary answers are selected.

By using priorities and concentration limits a final answer is selected for each element.

The final answers are saved until the 10th sample, or the last sample of a group, or the last spectrum is recorded, at which time a report form is printed (fig.1).

Each spectrum on the plate is recorded as a file on tape. A 2,400-foot reel of tape (7 track) recorded at a density of 800 bits per inch with records of 1,500 digits (binary coded decimal) in length is ample for recording an entire plate having a maximum of 40 spectra. The first record in each file is 12 digits long and is used for identification purposes. Each succeeding record is a set of 500 three-digit numbers (10 times percent transmittance) with all digits being significant when re-recording the same spectrum.

Large variations in the spectrographic analysis of a sample can always be expected. These variations are minimized by rigidly controlling both the methods of sample preparation and the exposure conditions, including an argon-oxygen atmosphere, and by careful plate development.

Correlating the line position in the spectrum with the transmittance reading in the recording is accomplished by starting the recording at a known position and by counting the readings thereafter. This assumes a reasonably constant dispersion of the spectral lines on the plate, and assumes no missed readings during the digitizing-recording step. The possibility of an occasional missed reading caused by input-ouput errors is ever present. However, the programed error-handling procedure has effectively taken care of all input-output errors encountered thus far.

Each digit of the first record, 12 digits long, in each file is entered manually by using a thumb-wheel switch. The first field within the fixed data (table 3) is designated by the symbolic name ICODE and identifies the type of spectrum from which the transmittances following it have been recorded. There is, in addition, a fixed order in which the spectra are recorded on the tape. The unfiltered step of the split-filter iron calibration spectrum is recorded first and is followed by the filtered step. The variable TPCT (type of plate calibration treatment), which is read in from a card (table 1) and becomes the first digit of the program number, provides a means for bypassing routine plate emulsion calbration curve treatment by reading in coefficients.

Standards may be run as samples, the difference being they will not appear on the report form. An ICODE of "61" is entered for the last sample of a grouping, and a report form will be printed including that file but not the next file; it

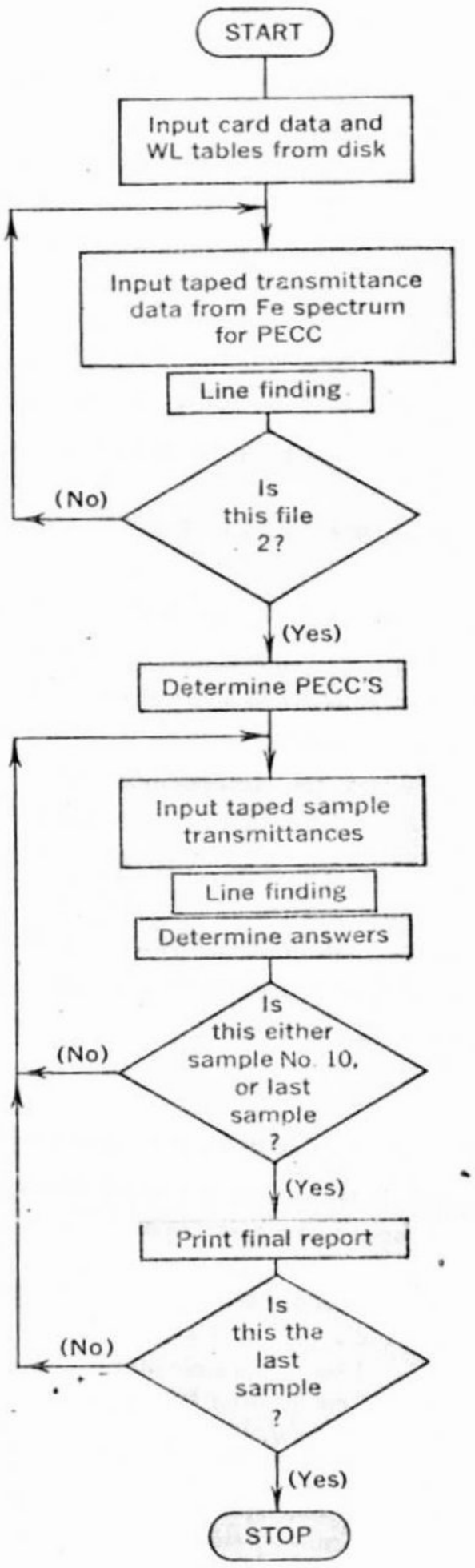


Figure 1.–Flow chart of major functions of the final emission spectrographic analysis computer program. WL, wavelength; PECC, plate emulsion calibration curves.

means that a card is to be read which contains information for the next report form. After the last full spectrum is recorded one additional short file is recorded consisting of a set of fixed data, the first digit of which must be an "8" followed by at least one full record of transmittance data. This "8" signals the end of the recording. However, the variable NF (number of files to read) read in on a card provides the option of not reading the entire recording. Similarly NRR (number of records to read from each file) makes possible the reading of a tape having no end-of-file marks.

Table 3.—*Types of fixed data*

Field	Number of digits	Description	Symbolic name
		Iron spectrum (unfiltered) ICODE 1	
1	1	Identification code	ICODE
2	3	Plate number	PLANO
3	2	Month recorded	IMO
4	2	Day recorded	IDA
5	2	Year recorded	IYR
6	2	Spectrum number on plate	NOSPEC
		Iron spectrum (filtered) ICODE 2	
1	1	Identification code	ICODE
2	4	Page number in recording book	PGNO
3	4	Transmittance of less-filtered part of split filter.	IPCTU
4	3	Transmittance of more-filtered part of split filter.	IPCTF
		Standards ICODE 31	
1	2	Identification code and internal standard treatment.	ICODE
2	6	Concentration (percentage element $\times 10^6$).	ICONC
3	2	Number of file being recorded	FINO
4	2	Spectrum number on plate	NOSPEC
		Unknowns [1] ICODE 41	
1	2	Identification code and internal standard treatment.	ICODE
2	6	Sample number	NOSAMP
3	2	File number being recorded	FINO
4	2	Spectrum number on plate	NOSPEC

[1] ICODE 41 is used if a report form is intended, ICODE 51 if not.

FEATURES

Line finding

The line-finding procedure as presently programed for routine use is an efficient but not restrictively rigid method. Estimated positions (EP's) are read in for all lines as part of the wavelength table. A line is recognized by first searching for a minimum transmittance among 11 readings, 5 on each side of the EP. A peak is defined as the transmittance which is at least 0.2 percent less than that of the readings on each side. If more than one reading differs by less than 0.2 percent the peak is considered to have a flat top. A peak is too flat if it is more than five readings wide. The position of the peak is the position of the minimum transmittance unless it has a flat top; if so, it is the midpoint (rounding toward the EP). If two legitimate peaks are found within the search area, the darker of the two is chosen. To be considered as a possible answer, the peak position must be located within two readings of the EP. Also, it must fit the program definition of a line—that is, the transmittance difference between peak and background must be at least 1 percent.

A well-established starting point must be known before commencing the line-finding procedure. The method used to find lines in the iron spectra differs from that used in other spectra by the method of determining both the spread correction and the zero position. Both methods, however, have all the transmittances recorded for the spectrum in core storage at one time throughout the line-finding procedure.

The first minimum transmittance that is less than 80 percent and is within the first 30 readings of the iron spectra must be the peak of a known line. It may be either the Fe 2327.394, Fe 2331.307, or Fe 2332.797 line (or the Cd 2288 line). The variable NFL (number of first lines), which may equal 1 through 4, is read in on a card and identifies which of these four lines to expect—beginning with Cd 2288 if NFL=4, or on to Fe 2332 if NFL=1, and similarly with NLL (number of last lines). Whatever the choice, the position from which all the remaining lines are measured is the position of the peak of the Fe 2332 line, which by definition is zero in all spectra. For determining the stretch correction, the average of the positions of all the first lines used is taken as the lower boundary. By measuring from the position of the 2332 line, the estimated positions of the several last lines are used to find the Fe 4665.594, Fe 4662.609, and Fe 4654.785 lines. After the lines are found, their actual positions are averaged, thus providing the upper boundary for the stretch determination. The number of readings between the upper and lower boundaries is calculated and any spread correction is determined by comparison with the spread assumed when estimated positions were calculated. Any difference is corrected if its absolute value is less than 10—if more than 10 the spectrum is skipped.

For spectra other than those for plate calibration, the first line to search for is the Cd 2748 line. Two sections of the spectra are masked to permit the centering of cadmium lines 2748 and 4415, and these two lines serve for making any spread correction and for line finding. The recording of these spectra commences at approximately the same position as the iron calibration spectra. The Cd 2748 line is located by finding the first peak darker than 80 percent between readings 16,080 and 16,480, if recorded from our plates. Once the Cd 2748 line has been located, the Cd 4415 line is the first peak found between reading 64,920 (from the Cd 2748) and the next 100 readings. The number of readings between cadmium lines 2748 and 4415 is determined and compared with the expected difference. This comparison becomes the basis for making any spread correction that may be needed. The position zero for these spectra is taken as 16,105 readings below the Cd 2748 position.

The basic estimated position which is read in for each line is never permanently changed by the program but may be altered temporarily for a single spectrum when the need for it is indicated by the measurement of the length of the spectrum. A spread correction is made on estimated positions for any deviation of 10 or less from the expected distance as follows: The spectrum is divided into the number of sections which equals one more than the absolute value of the correction itself. The length of each section in readings is determined by dividing the number of sections into 90,000. The correction made in the first section is zero, and the correction for each

succeeding section advances by one until the correction in the last section is the full value of the spread correction, which is applied through reading 100,000. Each basic estimated position is temporarily adjusted at the time of line finding to produce the estimated position appropriate for the spectrum being analyzed.

Background and interferences

The background is determined by calculating from a straight line the value directly under the EP (estimated position). The straight line is formed by connecting two points, one on each side of the EP. The points are the maximum transmittances within 100 readings (2.5 A) of the EP. In the event of equal maximum transmittances, the one nearest the EP is used. The program adequately corrects for background. Other interferences such as interelement effects are being investigated, and the program will be modified to correct for these.

For routine use of the program the fewest possible interference treatments are being used. At present only three very simple ones are in the program, and these are applied only after temporary answers have been chosen. Many gross interferences are effectively handled by means of the priority number concept when selecting temporary and final answers. The entire basis of answer selection lies in the proper application of the priority concept. The priority-one line is the most sensitive line which is relatively interference free. The priority-two line is a little less so on both counts, and similarly down the unbroken priority sequence. After the continuity is broken by skipping priority number, priorities may be assigned indiscriminately through 99 for any purpose desired. Answers are selected only from the unbroken sequence of priorities beginning with priority one. By definition, as priorities increase, the assigned concentration limits never decrease while in the unbroken sequence. Those beyond the skipped priority are unaffected by these restrictions. The process of selecting answers starts with the priority-one line and ends with the last line in the priority chain. Any line having a peak transmittance less than 2.0 percent is too dark for evaluation and is skipped, as is any line producing an answer greater than the upper concentration limit of its analytical curve. The procedure for selection of answers is described further in the section "Final Answers and Report Form."

The investigation of interferences presently has top priority to upgrade many lines, thus making many more potential answers available. The three interference treatments being used now generally perform as follows:

1. If the final answer for iron is above 13 percent, an answer from the K 4047 line is unacceptable.
2. If either magnesium, iron, or chromium is above a certain concentration (a different concentration for each), a sodium answer is accepted from only its priority-one or priority-two lines.
3. If neither platinum nor palladium is present, osmium, iridium, ruthenium, and rhodium are reported as less than their lower limits.

The variable NI (number of interferences) which is read in from a card and which is the last digit of the program number, simply indicates the number of interference subroutines in the program.

Plate emulsion calibration curve

The plate emulsion calibration curve (PECC) relates percentage transmittance to intensity. The method chosen for this work utilizes the change in transmittance of a line as measured from each step of a single iron burn exposed through a two-step (split) filter. A total of 219 iron lines is found in each step, and by pairing the transmittance of a line from the most filtered step of the two-step iron exposure (T_F) with its transmittance from the least filtered step (T_U) a point is defined for the preliminary calibration curve, a second-degree curve, (fig. 2). A different curve is determined for use over a 250-A range by using data from 26 lines which permits a few overlapping lines for each. By including an additional two points, one on each end weighted 26 times, the curve is well controlled without actually being forced. The weighted points are (1.0, 1.5) and (99.0, 100.0), thus providing 78 points to be fitted with the abscissa, ln T_U, being the independent variable and the ordinate, ln T_F, the dependent variable. The generic equation is $y=ax^2+bx+c$ with a always negative and y greater

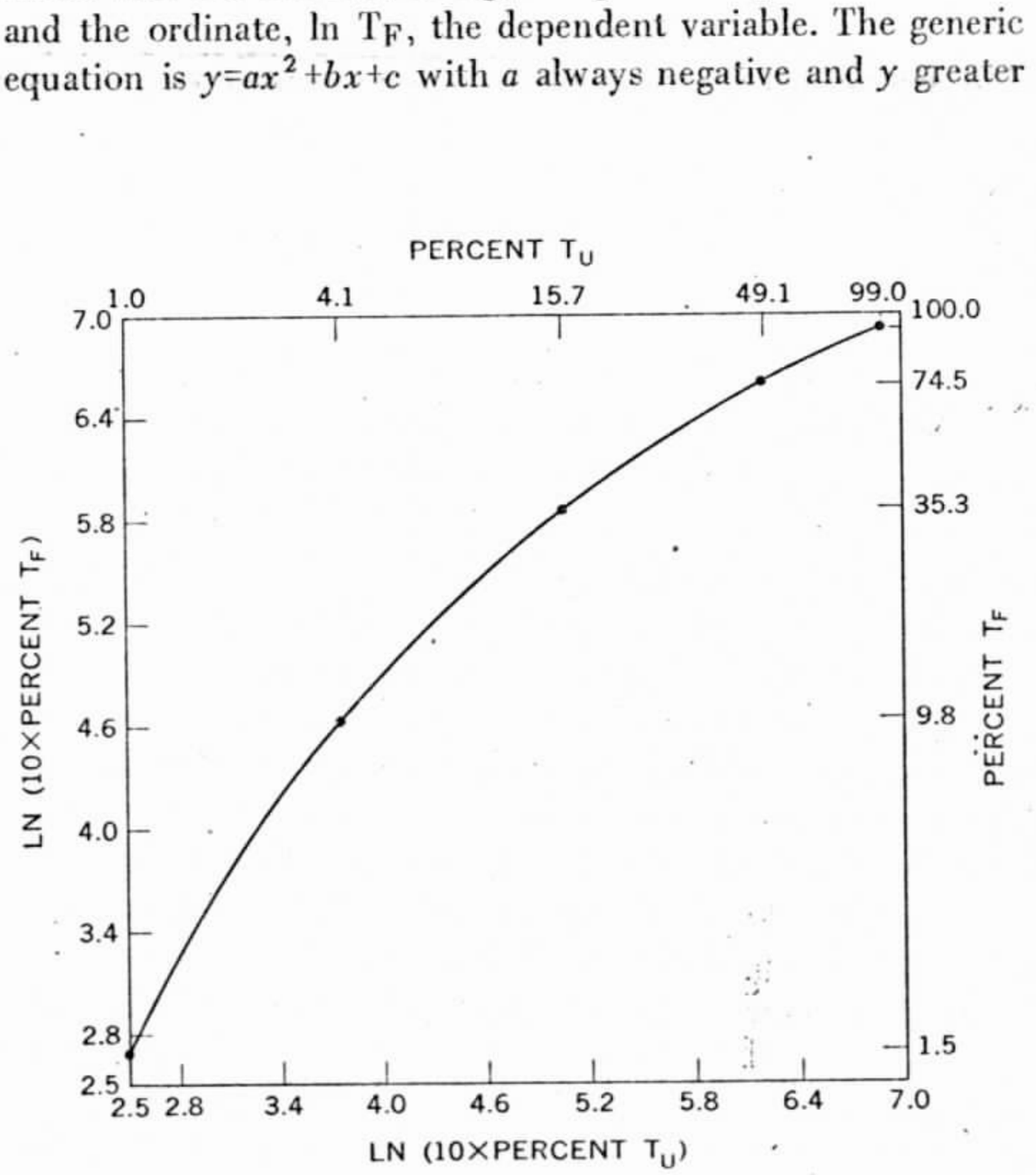


Figure 2.–Preliminary plate emulsion calibration curve relating transmittance from the unfiltered step, T_U, to the filtered step, T_F.

than x. This fitted curve provides the ordinate component, the natural logarithm of the percentage transmittance, of the points for the final PECC. The natural logarithm of the filter factor provides the abscissa component of the points (equally spaced along the x-axis). The filter factor (about 2) is the ratio of the percentage transmittances of the unfiltered half of the filter and the filtered half of the filter. A few selected points are identified in figure 2.

Points for the final plate emulsion calibration curve (PECC) (fig. 3) are obtained as follows: The first point obtained from the preliminary PECC is called the inflection point (IP) of the final PECC. It is defined as that point near the 45° slope point on the preliminary PECC which will produce the first calculated point above it at the same distance away as the first calculated point below it. To select points above the IP, the y component of the IP is substituted into the preliminary PECC equation as x and a new y is calculated. This y is substituted into the equation as x, and this continues until a new y exceeds 6.86 (ln 10×95.4 percent transmittance). At this point, y is increased regularly at the rate of 0.01 (about 1 percent transmittance) per point until it exceeds ln 10×100 percent, this point being set equal to ln 10×100 percent. To select points below the IP, the x component is substituted into the equation as y and a new x is calculated. This continues until a new x is calculated which is less than 1 percent transmittance. This is the lowest point calculated.

The inflection point is placed on an imaginary line having a slope of 315° and passing through the point ln 10 percent transmittance and ln 100,000 intensity. The final PECC is built from the inflection point in both directions. The preliminary PECC provides a most accurate and convenient measure of the relative change in transmittance. This nicely smoothed and averaged measure of transmittance change provides an excellent source of points to be used with the natural logarithm of the ratio of the split-filter transmittances. The points of the final PECC produce a curve generally S-shaped but one which cannot be adequately represented by a cubic equation. An algorithm is used in the program utilizing the preliminary PECC quadratic with the natural logarithm of the filter factor producing an "exact fit" final PECC. This permits all the averaging and fitting to remain in the preliminary PECC which utilizes the newly measured quantites. All the points initially obtained from a preliminary PECC for the final PECC are shown in figure 3.

Element concentration calibration curves

To prepare the element concentration calibration curve (ECCC), separate programs are used which perform the entire job for many curves and most of the work required in the

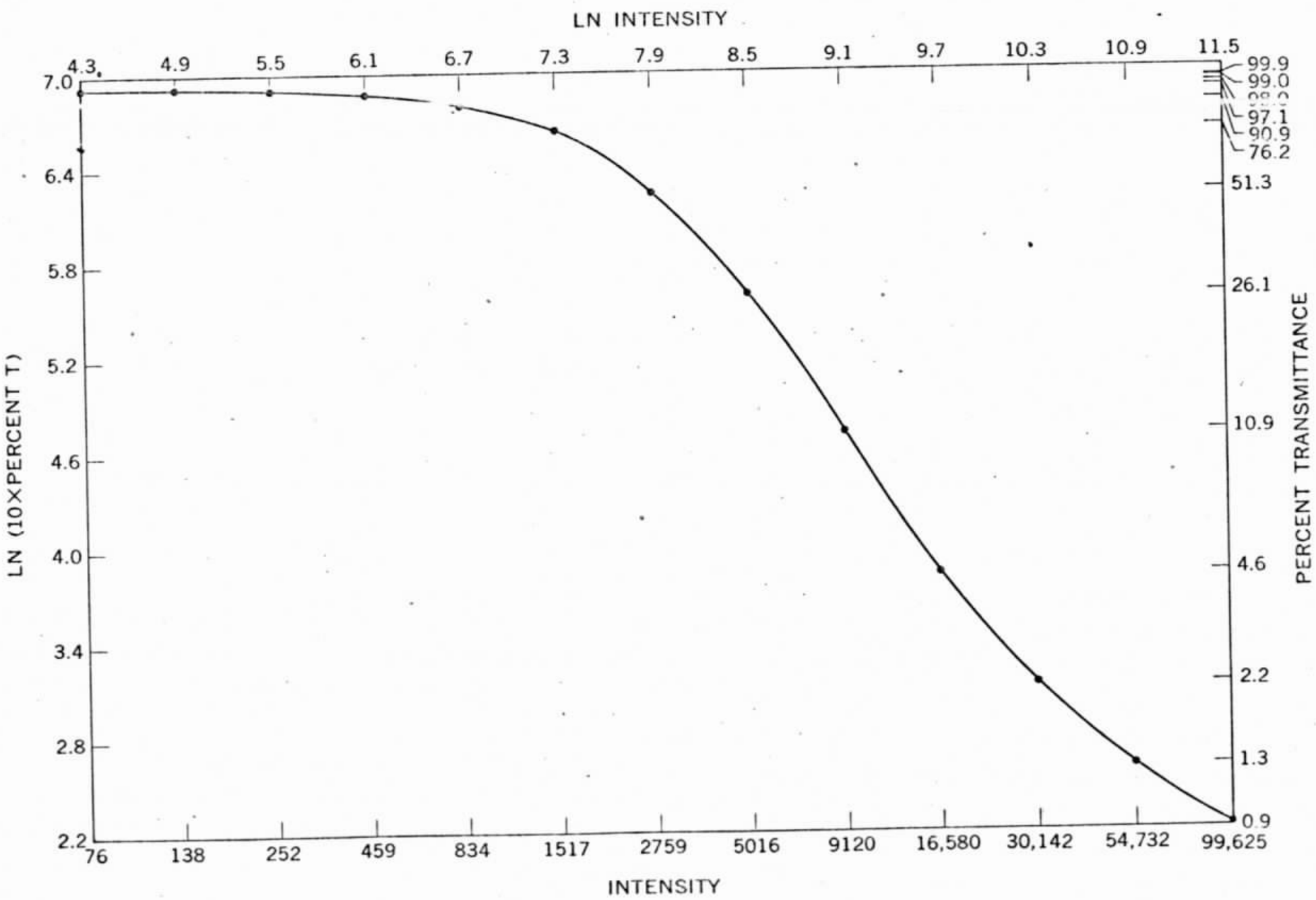
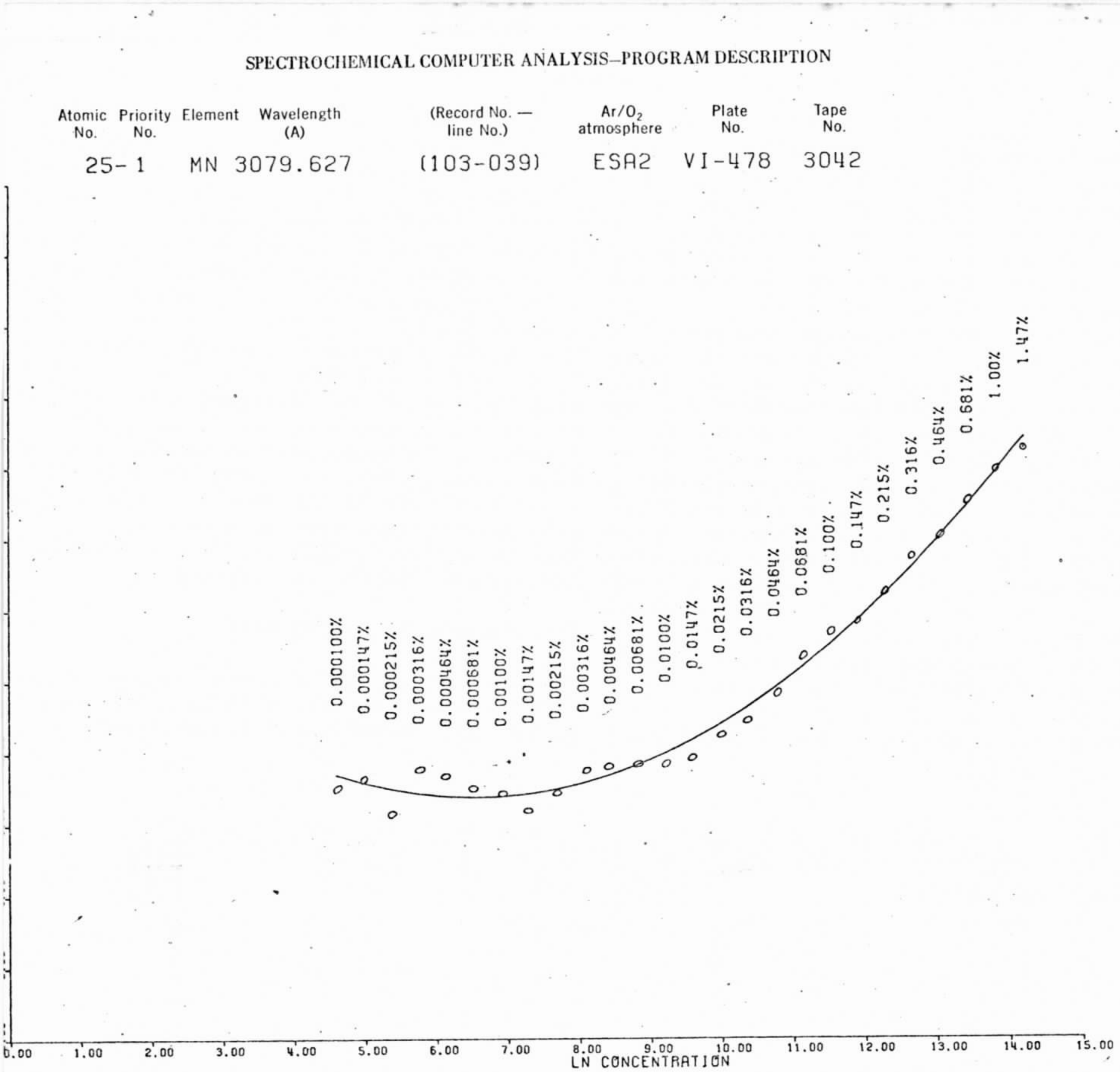


Figure 3.—Final plate emulsion calibration curve relating intensity to transmittance.

Atomic No.	Priority No.	Element	Wavelength (A)	(Record No. — line No.)	Ar/O_2 atmosphere	Plate No.	Tape No.
25	1	MN	3079.627	(103-039)	ESA2	VI-478	3042

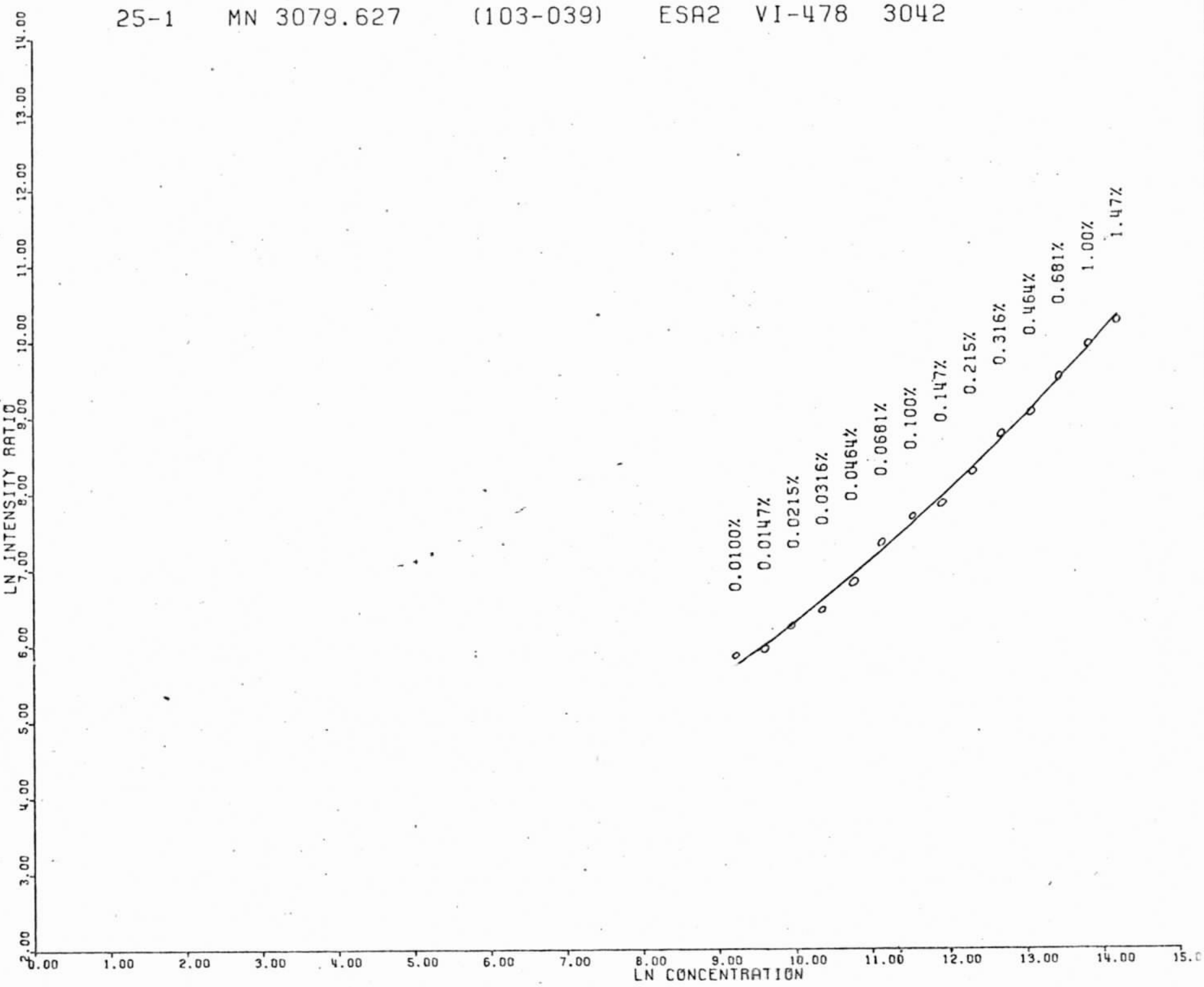


A

Figure 4.—Element concentration calibration curves using a Mn 3079.627 line plot as an example. *A*, first fitting (without limits); *B*, second fitting (with limits).

preparation of the others. Standards are prepared to give six evenly divided points between orders of magnitude of concentration (Myers, and others, 1961). Transmittances from these standard spectra are recorded on magnetic tape in order of descending concentration. A search for analytical lines from the wavelength table is made in each file of transmittances, and selected data from all standard spectra are printed. After this is completed, all the data accumulated for each line are evaluated and the resulting points are fitted by the PS (point selecting) program. A second-degree curve is the highest degree fitted, and two of these fittings are accomplished for each line—one without limits and one with limits (fig. 4). The first fitting, without limits, omits points taken from a record having an input-output error (that is, the entire record is skipped), any with a peak-background difference of less than 1 percent transmittance, those with a peak transmittance of less than 2 percent (too dark), and data from any blank or matrix spectrum (that is, concentration equals zero). A limited statistical study and an analysis of variance are made for each fitting, and a table of raw points and smooth points with residuals is also prepared for the highest degree fitted. The second fitting, with limits, fits only those points remaining by examining points starting with the highest concentration and using all with regularly decreasing intensities.

Atomic No.	Priority No.	Element	Wavelength (A)	(Record No.—line No.)	Ar/O_2 atmosphere	Plate No.	Tape No.
25-1		MN	3079.627	(103-039)	ESA2	VI-478	3042



B

Figure 4.

Statements are included which provide for the preparation of a tape for use by the CalComp plotter. Both curves, without and with limits, are plotted, each producing a plot 7 by 10 inches. These dimensions may be altered by changing only one program card. Provision is made for printing full identification of the curve on the plot.

If the second-degree fit is better than the straight-line fit, both sets of coefficients are available. The first-degree fitting is not classified. However, the evaluation for the second-degree fitting proceeds as follows:

Class 0, if <3 points are supplied for fitting,
1, for 3 points, and
2, for 4 points if the standard deviation (sd) is greater than 0.5.

Beyond this, the value of the class may range up to a maximum of 10 as shown in the following calculation:

Class = (points factor + sigma factor + residual factor)/3, where

Points factor = 4 if there are 4 points to fit, or
= 10 for 5 or more points, and

Sigma factor = 6 if there are 4 points to fit, or
= 1 if sd >0.9, or
= 10 - 10.0 × sd, and

Residual factor = 10 × (fraction of points having a residual ≤0.1).

EMISSION SPECTROGRAPHIC ANALYSIS PAGE 1-A

REPORT 72-WSH-00 PROGRAM NO. 203 FOR: GEORGE G. GEOLOGIST A. B. CHEMIST (ANALYST)
JOB NO. 11223344 PLATE NO. VI-6789 DATE: 12/21/72 P. S. LEADER (PROJECT LEADER)
GROUP NO. 123456 RECORDING NO. 987

FIELD NO. SAMPLE SPECTRUM		W-999990 2	W-999991 3	W-999992 4	W-999993 5	W-999994 6	W-999995 8	W-999996 9	W-999997 10	W-999998 11	W-999999 12
SI	%	17.8	17.9	19.8	18.5	21.7	19.5	17.9	21.8	19.6	18.9
AL	%	6.10	6.23	6.73	7.25	7.87	6.56	6.33	8.03	7.65	7.87
FE	%	10.4	8.33	9.30	7.50	8.93	9.53	9.81	8.82	9.86	9.23
MG	%	6.50	6.74	6.92	6.73	7.64	6.40	5.68	6.23	6.62	6.41
CA	%	4.85	4.98	5.63	5.99	7.12	6.14	5.59	5.65	5.94	5.99
NA	%	> 0.316	> 0.316	> 0.316	> 0.316	> 0.316	> 0.316	> 0.316	> 0.316	> 0.316	> 0.316
K	%	0.695	< 0.0681	0.230	0.383	0.355	0.463	0.545	0.539	< 0.0681	0.248
TI	%	1.34	0.573	0.446	0.464	0.603	0.781	0.870	0.968	0.434	0.933
P	%	0.703	0.101	< 0.0464	0.140	< 0.0464	0.293	0.425	0.369	< 0.0464	0.172
MN	%	0.201	0.156	0.167	0.153	0.177	0.171	0.182	0.164	0.176	0.186
AG	PPM	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10
AS	PPM	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100
AU	PPM	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81
B	PPM	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0
BA	PPM	403	109	141	181	180	223	300	396	133	170
BE	PPM	1.35	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00
BI	PPM	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00
CD	PPM	< 14.7	< 14.7	< 14.7	< 14.7	< 14.7	< 14.7	< 14.7	< 14.7	< 14.7	< 14.7
CE	PPM	166	< 20.0	< 20.0	< 20.0	< 20.0	< 20.0	101	115	< 20.0	< 20.0
CO	PPM	45.1	44.9	51.7	40.8	52.8	47.0	42.8	42.2	58.8	57.5
CR	PPM	137	212	488	255	469	240	157	206	288	115
CS	PPM	< 3160	< 3160	< 3160	< 3160	< 3160	< 3160	< 3160	< 3160	< 3160	< 3160
CU	PPM	51.5	19.1	46.4	24.2	47.4	45.4	46.5	56.5	56.0	66.7
DY	PPM	9.77	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	9.14	< 3.16	< 3.16
ER	PPM	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15
EU	PPM	3.07	< 1.00	< 1.00	1.08	< 1.00	1.80	2.53	2.52	< 1.00	2.00
GA	PPM	14.9	6.45	7.16	7.41	9.17	12.7	14.5	15.5	8.16	13.5
GD	PPM	12.1	5.04	6.31	-5.32	4.82	4.62	5.55	4.46	5.06	7.28
GE	PPM	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00
HF	PPM	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0
HG	PPM	< 147	< 147	< 147	< 147	< 147	< 147	< 147	< 147	< 147	< 147
HO	PPM	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00	< 1.00
IN	PPM	< 4.64	< 4.64	< 4.64	< 4.64	< 4.64	< 4.64	< 4.64	< 4.64	< 4.64	< 4.64
IR	PPM	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81
I	PPM	40.9	< 14.7	< 14.7	< 14.7	< 14.7	< 14.7	26.8	35.2	< 14.7	< 14.7
LI	PPM	< 31.6	< 31.6	< 31.6	< 31.6	< 31.6	< 31.6	< 31.6	< 31.6	< 31.6	< 31.6
LU	PPM	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16
MN	PPM	2010	1560	1670	1530	1770	1710	1820	1640	1760	1860
MO	PPM	4.77	3.89	7.87	3.96	10.2	3.67	3.98	6.01	7.39	6.05
NB	PPM	30.1	2.42	4.98	5.10	8.36	7.54	11.6	20.6	4.78	11.8
ND	PPM	H	< 14.7	< 14.7	17.2	H	< 14.7	34.9	< 14.7	< 14.7	< 14.7
NI	PPM	57.8	91.0	147	91.0	208	93.8	60.2	72.8	122	111
CS	PPM	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5
PB	PPM	7.29	1.11	2.63	3.85	2.91	5.28	4.85	5.72	3.14	4.60
PD	PPM	< 0.22	< 0.22	< 0.22	< 0.22	< 0.22	< 0.22	< 0.22	< 0.22	< 0.22	< 0.22
PR	PPM	H	< 2.15	H	6.46	H	7.63	10.1	10.5	H	H
PT	PPM	< 2.15	< 6.81	< 2.15	< 2.15	< 2.15	< 6.81	< 2.15	< 2.15	< 2.15	< 2.15
RB	PPM	< 14700	< 14700	< 14700	< 14700	< 14700	< 14700	< 14700	< 14700	< 14700	< 14700
RE	PPM	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0
RH	PPM	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10		< 0.10
RU	PPM	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46	< 0.46
SB	PPM	< 68.1	< 68.1	< 68.1	< 68.1	< 68.1	< 68.1	< 68.1	< 68.1	< 68.1	< 68.1
SC	PPM	26.9	29.5	40.4	34.8	> 46.4	31.4	27.8	35.7	42.0	41.8
SM	PPM	5.91	< 4.64	< 4.64	< 4.64	< 4.64	< 4.64	< 4.64	< 4.64	< 4.64	< 4.64
SN	PPM	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16
SR	PPM	324	179	196	242	233	286	358	376	187	269
TA	PPM	< 147	< 147	< 147	< 147	< 147	< 147	< 147	< 147	< 147	< 147
TB	PPM	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81	< 6.81
TE	PPM	< 316	< 316	< 316	< 316	< 316	< 316	< 316	< 316	< 316	< 316
TH	PPM	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5	< 21.5
TL	PPM	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16	< 3.16
TM	PPM	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15	< 2.15
U	PPM	< 215	< 215	< 215	< 215	< 215	< 215	< 215	< 215	< 215	< 215
V	PPM	345	281	317	308	336	337	290	306	333	343
W	PPM	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0	< 10.0
Y	PPM	53.5	14.7	18.8	16.4	19.9	25.2	34.8	36.5	17.8	29.3
YB	PPM	6.48	2.29	2.63	2.64	3.21	3.93	4.62	4.16	2.96	4.59
ZN	PPM	193	108	124	110	119	152	173	145	115	130
ZR	PPM	629	86.9	120	112	184	156	256	293	94.0	217

MAJORS RECALCULATED AS OXIDES

SIO2	%	38.1	38.2	42.3	39.6	46.4	41.6	38.3	46.6	41.9	40.5
AL2O3	%	11.5	11.8	12.7	13.7	14.9	12.4	12.0	15.2	14.5	14.9
FE2O3	%	14.8	11.9	13.3	10.7	12.8	13.6	14.0	12.6	14.1	13.2
MGO	%	10.8	11.2	11.5	11.2	12.7	10.6	9.42	10.3	11.0	10.6
CAO	%	6.78	6.97	7.88	8.38	9.97	8.59	7.82	7.90	8.31	8.38
NA2O	%	> 0.426	> 0.426	> 0.426	> 0.426	> 0.426	> 0.426	> 0.426	> 0.426	> 0.426	> 0.426
K2O	%	0.837	< 0.0820	0.278	0.462	0.428	0.558	0.656	0.650	< 0.0820	0.299
TIO2	%	2.23	0.955	0.744	0.774	1.01	1.30	1.45	1.61	0.725	1.56
P2O5	%	1.61	0.231	< 0.106	0.321	< 0.106	0.671	0.973	0.844	< 0.106	0.393
MNO	%	0.259	0.202	0.215	0.198	0.229	0.221	0.235	0.212	0.227	0.240

Figure 5.—Example of an emission spectrographic analysis report printout.

Also calculated are the points on the curve where the slope is 50° and where it is 30°. This information defines the best section of the curve. All these calculations are most useful when assigning priorities.

The program suggests upper and lower concentration limits for those second-degree curves fitted with limits. The upper limit is the highest concentration with a peak transmittance ≥2 percent, and a tangent slope ≥0.3 (16.7°). The lower limit is the lowest concentration with a tangent slope ≥0.3 (16.7°) but with an intensity no less than that of any lower concentration.

A knowledge of possible interferences is necessary when making the initial selection of lines for fitting. After the points are fitted and the plots are visually examined, the fitting statistics are considered and the coefficients are put into the wavelength table. The lines and curves are further evaluated on the basis of the results from different samples and standards before being assigned a priority in the chain. Considered in selection of lines are general reliability for producing right answers, the existence of an effective interference correction if the need for one is indicated, and the possibility of making the line useful, if by changing concentration limits, some interference corrections can be bypassed.

FINAL ANSWERS AND REPORT FORM

After the line finding has been completed by the final program, the transmittances are converted to intensities and the background is subtracted from the peak. This intensity difference is substituted into the appropriate element concentration calibration curve, and the equation is solved. Three types of answers obtained by this program are preliminary, temporary, and final. A preliminary answer of some kind is assigned each line. Some of the lines at this time may have several preliminary answers assigned because of certain recognized error conditions. Preliminary answers possible are:

- −1 = input-output error,
- −2 = no coefficients,
- −3 = no peak but EP<2 percent transmittance,
- −4 = no peak but EP≥2 percent transmittance,
- −5 = peak too flat,
- −6 = peak too far away from EP,
- −7 = peak minus background <1 percent transmittance,
- −8 = peak too dark,
- −9 = equation unsolvable (below vertex),
- −10 = equation unsolvable (above vertex).

The temporary answer for the line is selected from among the several preliminary answers for the line.

The answer selected as the temporary answer is the first one found in the order −1 to −10. All final answers are selected from these temporary answers by examining them in the order of the preassigned priority numbers which were read in as part of the wavelength table. The final answer accepted is the first answer less than the assigned lower limit or the first answer falling between the limits. Any answer examined greater than its upper limit permits the examination of the line next in the priority chain. Temporary negative answers treated as less than the lower limit answers are −4, −6, −7, and −9. Those treated as greater than the upper limit answers are −8, and −10. The −1, −2, −3, and −5 answers are skipped during examination of the answers.

Final answers may be altered at this point only if less than a 15-mg sample was used or if an interference treatment is applicable. The value of the variable NFAMBF (table 1) is the number of samples less than 15 mg weight.

All the final answers determined for a spectrum are stored until the report is printed. A report (fig. 5) is printed at the first occurrence of 10 samples saved for printing, end of job, or last file on tape. All necessary identification data are printed on the report except the field number which is assigned by the geologist for his own convenience; a space is provided for the geologist to insert this.

Ten elements are defined as majors and are reported first as percentage element. The remaining 58 elements are reported as trace elements in parts per million. Manganese is reported as both a major and a trace for the convenience of geologists. The majors repeated at the bottom of the report have been recalculated as oxides for the convenience of those using data as oxides. The present format for the analytical report incorporates many suggestions received from many sources.

Additionally, a tape is prepared by writing each report form as a file on the tape. This provides for short-term storage for additional copies or for other purposes such as correction of erroneous input data.

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