

## **GSJ Optical Emission Direct-Reading Spectrograph for the Analysis of Geological Materials**

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### **Abstract**

An optical emission direct-reading spectrograph, which is specially designed for the analysis of major and minor elements of geological materials, was recently set up at the Geological Survey of Japan. Analytical programs, spectral lines and detailed specifications of the instrument are described. Applications to the analysis of geological materials are also demonstrated.

### **1. Introduction**

An optical emission direct-reading spectrograph: a direct-reader was recently set up at the Geological Survey of Japan for the analysis of a wide variety of geological materials. Up to 40 photomultipliers are installed in the GSJ direct-reader for a wide element coverage in the analytical specimens. Analytical programs, spectral lines and detailed specifications of the instrument are described.

The direct-reader was programmed for: silicate major (10 elements), silicate minor (11 elements), iron and manganese oxide (18 elements) and sulfide ore (14 elements) with five different kinds of internal standards and a mercury monitor.

Six basic excitation circuits are available: high voltage AC spark, DC arc, spark ignited uni-arc, spark ignited low voltage AC arc, high voltage AC arc and multisource.

Applications of the direct-reader to the geological materials have been reported by many workers (AHRENS and TAYLAR, 1961; ASTM, 1968; ANDO, 1965; DANIELSSON, LUNDGREN and SUNDKVIST, 1959; DANIELSSON and SUNDKVIST, 1959a, 1959b; GOVINDARAJU, 1960, 1963a, 1963b; HASLER, 1952; HASLER and BARLEY, 1952a, 1952b; MATSUMOTO, 1960; ROUBAULT, ROCHE and GOVINDARAJU, 1962/1963; SCHWANDER and MARLING, 1967; THOMPSON and BANKSTON, 1969; UNITED NATIONS, 1963; VOROB'EV and RUSANOV, 1964).

### **2. Instrumentation**

#### **2.1 Direct-reader**

The direct-reader is a Nippon Jarrel-Ash "Compact Atomcounter" model 66000, a concave grating spectrograph with an electronics system.

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Spectrograph

Mounting: 1.5 m Paschen-Runge  
 Grating: concave, 1200 groove/mm, replica  
 Wavelength range: 2000—8000 Å  
 Dispersion: 5.45 Å/mm (1st order), 2.7 Å/mm(2nd order)  
 Resolution: 0.2 Å  
 Entrance slit: 25 μm (width), vertical  
 Exit slit: 75 μm (width), vertical

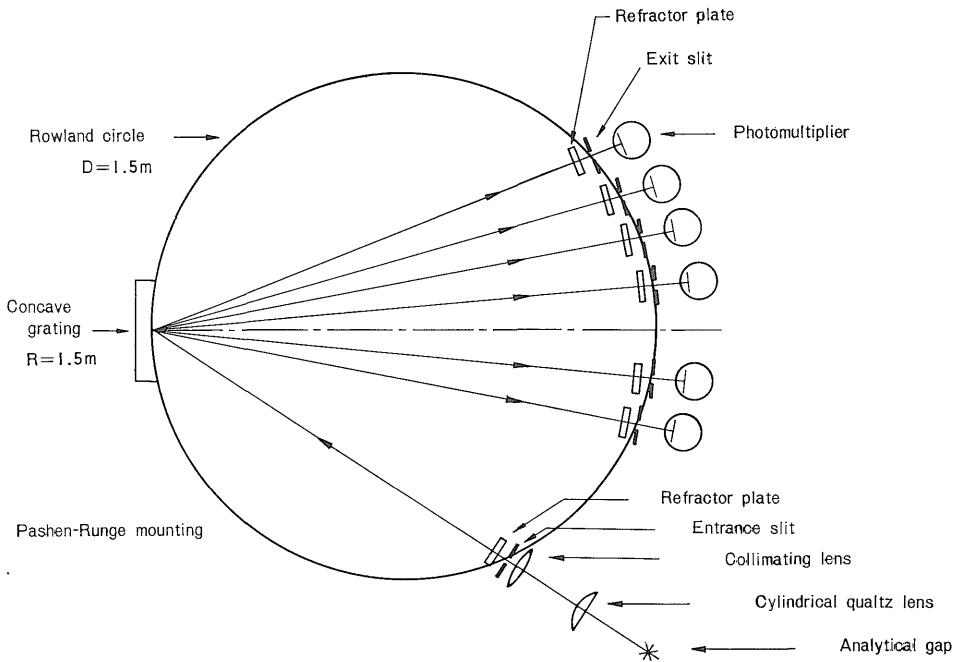


Fig. 1 Optical system, Compact Atomcounter.

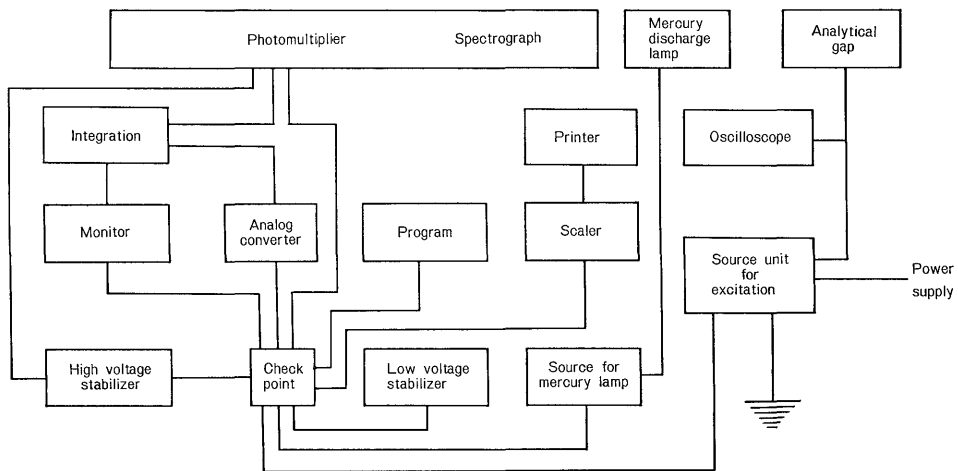


Fig. 2 Constitution of the Compact Atomcounter.

G SJ Optical Emission Direct-Reading Spectrograph (ANDO and IKEDA)

A light beam passes through the vertical entrance slit with refractor plate and to the grating. Exit slits with refractor plates are placed at the chosen wavelength positions on the focal curve of the spectrograph. Spectral energies are received by photomultipliers and integrated for a single exposure. Sequential readout electronics system permits the indication of integrated values both on a digital scaler (5 digits) and also on an automatic typewriter for up to 22 channels. An optical system is shown in Fig. 1 and a construction of the Compact Atomcounter in Fig. 2.

2.2 Analytical program

Four analytical programs: silicate major (A), silicate minor (B), iron and manganese oxide (C) and sulfide ore (D) are designed. Programs, wavelengths of both analytical and internal standard lines, and concentration ranges of analytical components are summarized in Table 1.

Table 1 Analytical program—1.

No.	Component <sub>o</sub> Wavelength(A)		Concentration range (%)			
			(A) Silicate major	(B) Silicate minor	(C) Iron & mang- anese oxide	(D) Sulfide ore
1	SiO <sub>2</sub>	2516 x 2	20 -80			
2	Al <sub>2</sub> O <sub>3</sub>	3961 x 2	0.5 -20			
3	Fe <sub>2</sub> O <sub>3</sub>	2599 x 2	0.5 -30			
4	MnO	2933 x 2	0.02- 5		1 -30	0.01-10
5	CaO	3158 x 2	0.6 -20			0.01- 5
6	MgO	2783	0.25-40			
7	TiO <sub>2</sub>	3685	0.1 - 5		0.1- 5	
8	P <sub>2</sub> O <sub>5</sub>	2149	0.1 - 1		0.1- 5	
9	Na <sub>2</sub> O	3302 x 2	0.1 -10			
10	K <sub>2</sub> O	4044	0.1 -10			
11	Ni	3414 x 2		0.0007-0.1	0.0007- 5	0.0007- 1
12	Co	3453 x 2		0.0007-0.1	0.0007- 5	0.0007- 1
13	Cr	4254		0.001 -0.1	0.001 - 5	
14	V	3202 x 2		0.0025-0.1	0.0025- 1	
15	Cu	3247 x 2		0.0003-0.1	0.0003- 1	0.0003- 1
16	Pb	3683 x 2		0.002 -0.1	0.002 - 1	0.002 - 1
17	Ba	5535		0.015 -1.0		
18	Rb	7800		0.001 -0.1		
19	B	2497		0.0025-0.1		
20	Zr	3391		0.0015-0.1		
21	As	2349			0.05 - 5	0.05 - 5
22	Zn	3345 x 2			0.05 - 5	0.05 - 5
23	Sn	2706			0.002 - 1	0.002 - 1
24	Si	2881			0.01 - 3	
25	Al	3944			0.01 - 3	
26	Mo	3170			0.001 - 1	
27	Mg	2798 x 2			0.0003- 1	
28	In	4511			0.001 - 1	0.001 - 1
29	Sb	2598				0.01 - 5
30	Bi	3067 x 2				0.001 - 1
31	Cd	3261				0.002 - 1
32	Ag	3280 x 2				0.0003- 1
33	Mn	2949			0.1 -25	
34	Sr	4607		0.0015-0.1		
35	Hg	4358	Monitor			
36	Li	4972 I	I.S.#5			
37	Sr	3380 II x 2	I.S.#4			
38	Co	4867 I	I.S.#3			
39	Pd	3481 I	I.S.#2			
40	Pd	2658 II x 2	I.S.#1			

Table 2 Analytical program—2.

Program (A) Silicate major

Element	Wavelength(Å)	Channel No.	Dynode No.
Si	2516 x 2	1	1
Al	3961 x 2	2	2
Fe	2599 x 2	3	3
Mn	2933 x 2	4	4
Ca	3158 x 2	5	5
Mg	2783	6	6
Ti	3685	7	7
P	2149	8	8
Na	3302 x 2	9	9
K	4044	10	10

Program (B) Silicate minor

Element	Wavelength(Å)	Channel No.	Dynode No.
Ni	3414 x 2	1	11
Co	3453 x 2	2	12
Cr	4254	3	13
V	3202 x 2	4	14
Cu	3247 x 2	5	15
Pb	3683 x 2	6	16
Ba	5535	7	17
Rb	7800	8	18
B	2497	9	19
Zr	3391	10	20
Sr	4607	11	34

Program (C) Iron and manganese oxide

Element	Wavelength(Å)	Channel No.	Dynode No.
Ni	3414 x 2	1	11
Co	3453 x 2	2	12
Fe	2599 x 2	3	3
V	3202 x 2	4	14
Cu	3247 x 2	5	15
Pb	3683 x 2	6	16
Ti	3685	7	7
P	2149	8	8
As	2349	9	21
Zn	3345 x 2	10	22
In	4511	11	28
Mn	2949	12	33
Cr	4254	13	13
Sn	2706	14	23
Si	2881	15	24
Al	3944	16	25
Mo	3170	17	26
Mg	2798 x 2	18	27

Program (D) Sulfide ore

Element	Wavelength(Å)	Channel No.	Dynode No.
Ni	3414 x 2	1	11
Co	3453 x 2	2	12
Fe	2599 x 2	3	3
Mn	2933 x 2	4	4
Cu	3247 x 2	5	15
Pb	3683 x 2	6	16
Sb	2598	7	29
Bi	3062 x 2	8	30
As	2349	9	21
Zn	3345 x 2	10	22
In	4511	11	28
Cd	3261	12	31
Ag	3280 x 2	13	32
Sn	2706	14	23

Internal standard and monitor

Element	Wavelength(Å)	Channel No.	Dynode No.
Pd	2658 x 2	I.S.#1	40
Pd	3481	I.S.#2	39
Co	4867	I.S.#3	38
Sr	3380 x 2	I.S.#4	37
Li	4972	I.S.#5	36
Hg	4358	Monitor	35

## GSJ Optical Emission Direct-Reading Spectrograph (ANDO and IKEDA)

Table 3 Specifications of optical and photoelectric systems.

Element	Wavelength (Å)	Exit slit width, (μ)	Refractor plate*	Mirror type**	Channel No.				I.S.	Dynode No.	Photo-multiplier
					A	B	C	D			
P	2149	75	Q		8					8	HTV R 106
As	2349	75	Q				9	9		21	R 106
B	2497	75	Q			9				19	R 106
Sb	2598	75	Q	V				7		29	R 106
Sn	2706	75	Q				14	14		23	R 106
Mg	2783	75	Q	H	6					6	R 106
Si	2881	75	Q				15			24	R 106
Mn	2949	75	Q	V			12			33	R 106
Mo	3170	75	Q				17			26	R 106
Cd	3261	75	Q					12		31	R 106
Zr	3391	75	Q			10				20	R 106
Pd	3481	75	Q						#2	39	R 106
Ti	3685	75	Q		7		7			7	R 106
Al	3944	75	Q				16			25	R 106
K	4044	75	G		10					10	R 136
Cr	4254	75	G			3	13			13	R 106
Hg	4358	25	G	V					#Monitor	35	R 106
In	4511	75	G	H			11	11		28	R 106
Sr	4607	75	G				11			34	R 106
Co	4867	75	Q						#3	38	R 106
Li	4972	75	G	V					#5	36	R 106
Si	2516 x 2	75	C		1					1	R 106
Fe	2599 x 2	75	C		3		3	3		3	R 106
Pd	2658 x 2	75	C						#1	40	R 106
Ba	5535	75	G			7				17	931 A
Mg	2798 x 2	75	C	V			18			27	R 106
Mn	2933 x 2	75	C		4			4		4	R 106
Bi	3067 x 2	75	C					8		30	R 106
Ca	3158 x 2	75	C		5					5	R 106
V	3202 x 2	75	C			4	4			14	R 106
Cu	3247 x 2	75	C	V		5	5	5		15	R 106
Ag	3280 x 2	75	C					13		32	R 106
Na	3302 x 2	75	C	H	9					9	R 106
Zn	3345 x 2	75	C				10	10		22	R 106
Sr	3380 x 2	75	C	V					#4	37	R 106
Ni	3414 x 2	75	C			1	1	1		11	R 106
Co	3453 x 2	75	C	H		2	2	2		12	R 106
Pb	3683 x 2	75	C			6	6	6		16	R 106
Rb	7800 x 2	75	G			8				18	R 136
Al	3961 x 2	75	C		2					2	R 106

\*) Q:Quartz G:Glass C:Corax

\*\*) Reflection mirror type, V:vertical H:horizontal

A selector switch permits to select instantly up to five different kinds of internal standard lines for each analytical program. Li I 4972 Å is chosen for the volatile elements, atomic lines (Co I 4867 Å; Pd I 3481 Å) and ionized lines (Sr II 3380 Å; Pd II 2658 Å) are chosen for the arc and spark excitations as internal standard. Choice of spectral lines was made on the basis of reported data (literatures are mentioned in chapter 1).

Specification details with corresponding wavelengths are shown in Tables 2, 3. Arrangement of photomultipliers along the focal curve of the spectrograph is shown in Fig. 3. Four horizontal mirrors are used to deflect the light beam to the photomultipliers. Seven photomultipliers are hunged horizontally and vertical mirrors deflect up the light beam to the photomultipliers (Fig. 4). Other photomultipliers receive spectral energy directly without auxiliary separate mirrors. Number of photomultipliers: 40 is a nearly maximal limit for this spectrograph, hence best lines have not been chosen for some elements by the room limitation around the focal curve.

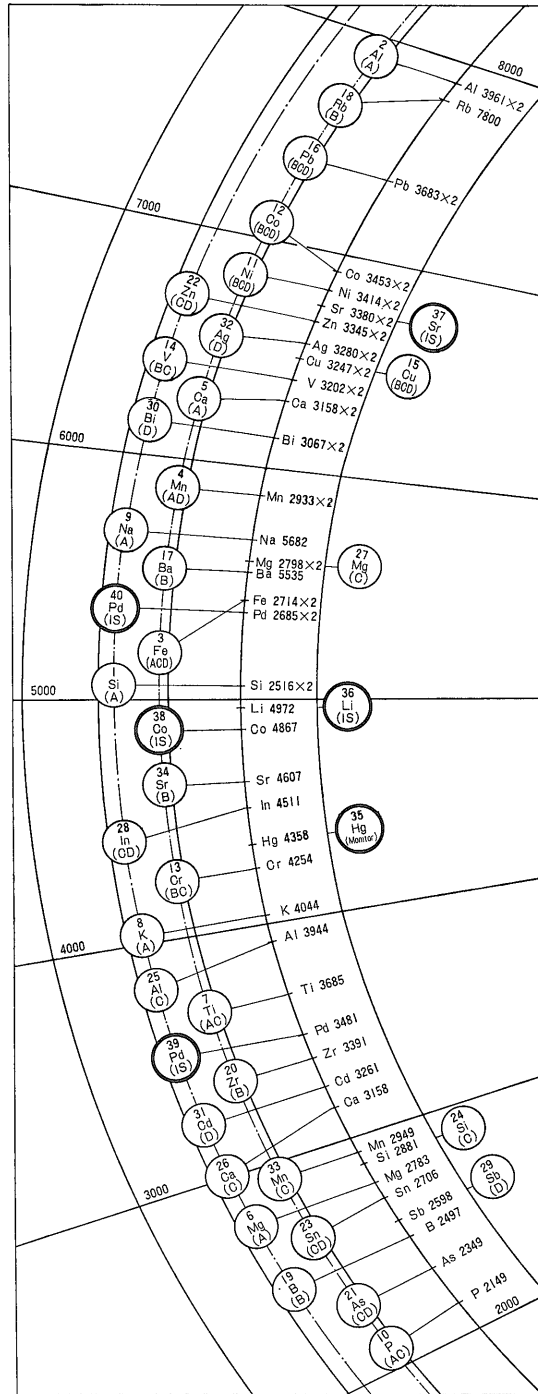


Fig. 3 Arrangement of photomultiplier.

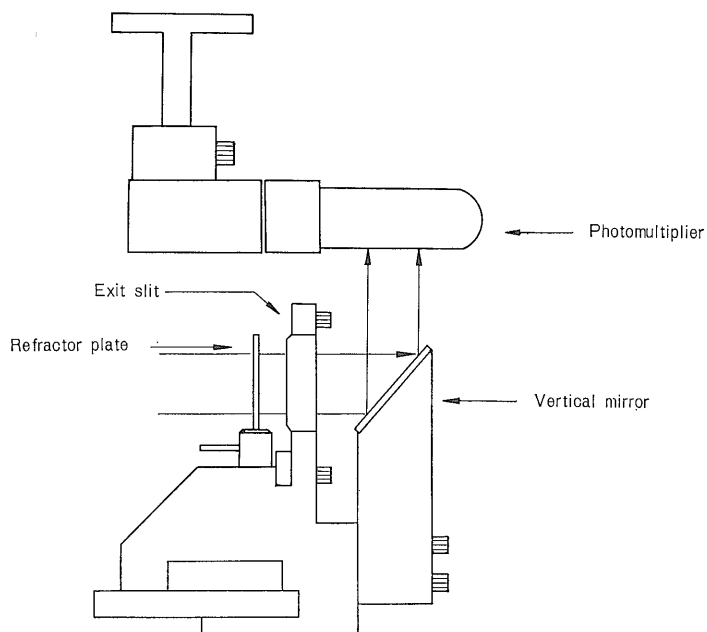


Fig. 4 Some photomultipliers are hung horizontally and vertical mirrors are used to deflect the light beam to the photomultiplier.

### 2.3 Excitation source

The Compact Atomcounter is installed combined with Jarrell-Ash Ebert 3.4 m plane grating spectrograph as shown in Fig. 5. Both varisource units in the direct-reader

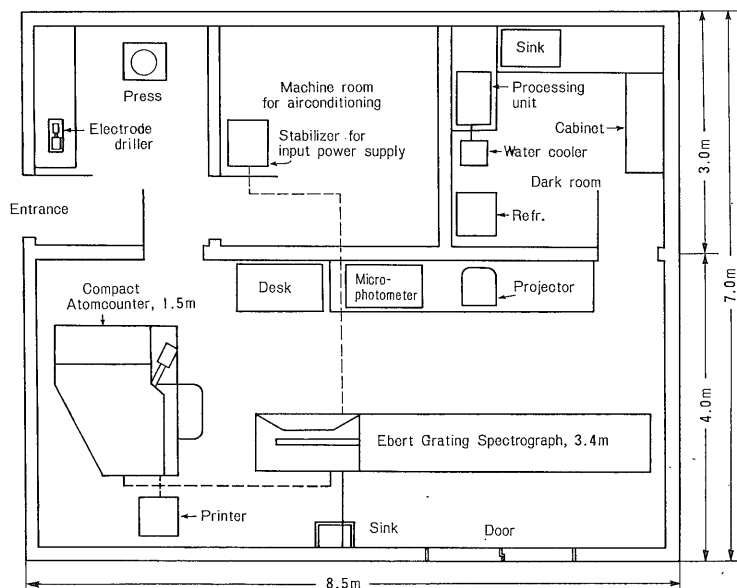


Fig. 5 Floor plan for a spectrochemical laboratory around a Ebert 3.4 m grating spectrograph and a Compact Atomcounter.

Table 4 Parameter specification of varisource units for the GSJ direct reader.

Nakanodenshi Multi-source Unit	
Multi-source	Input: Single phase, 200V Open circuit voltage: 1KV Inductance, microhenries: 50 and 360 Capacitance, microfarad: 2-60, controlled by combination of steps, 2, 5, 5, 10, 20 and 20 Resistance, ohms: 0-200, controlled by combination of steps, residual, 2, 3, 10, 10, 25, 50 and 100
Jaco Varisource Unit, Custom 4075	
High voltage AC spark	Input: Single phase, 230 V at 20 amps High voltage transforming rating: 7.5 KVA Primary voltage control: Variable auto transformer Open circuit secondary voltage: 31 KV peak Maximum continuous current: 20 RF amps Added primary resistance, ohms: 6 steps, 37-13 Secondary inductance, microhenries: 6 steps, residual, 40, 155, 310, 625 and 1250 Capacitance, microfarads: 5 steps, .0025, .005, .0075, .010 and .015 Secondary resistance, ohms: 4 steps, residual, 1, 2 and 3
DC arc	Input: Single phase, 230 V, 45 amps Open circuit terminal voltage: 280 V DC Output current rating: 2.5-30 amps Current control: Motor driven variable core reactor Ignition: Tesla coil AC ripple component: Average 3%
Spark ignited uni-arc	Input: Single phase, 230 V, 25 amps Open circuit terminal voltage: 280 V DC Output current rating: 1.0-8.0 amps Current control: 24 step resistor Ignitor: AC spark
Spark ignited low voltage AC arc	Input: Single phase, 230 V, 25 amps Open circuit voltage: 280 V Output current rating: 2.0-10.0 amps Current Control: 24 step resistor, 1/3 amp steps Ignition: AC spark
High voltage AC arc	Input: 230 V, 60 amps Open circuit voltage: 4800 and 2400 V Output current rating: 0.8-2.7 and 1.65-5.5 amps Current control: Motor driven variable core reactor Ignition: Tesla coil

side (Multisource, Nakanodenshi) and in the Ebert side (Jaco Custom 4075) are available. A selector switch permits to select up to six basic excitation circuits. Parameter specification of varisource units is given in Table 4.

### 3. Application to the analysis of geological materials

#### 3.1 Silicate major

Powdered rock sample (0.5 g) is mixed with a flux (2 g, Johnson Matthey spectrographic flux, a fused mixture of lithium tetraborate: 60%, strontium tetraborate: 30% and cobalt oxide: 10%) and funneled into a graphite crucible. A mixture is fused in a electric furnace at 1000°C for 5 minutes. After cooling a glass bead is easily pried from the bottom of crucible. The bead is crushed with a tungsten carbide mortars (Elis mortar



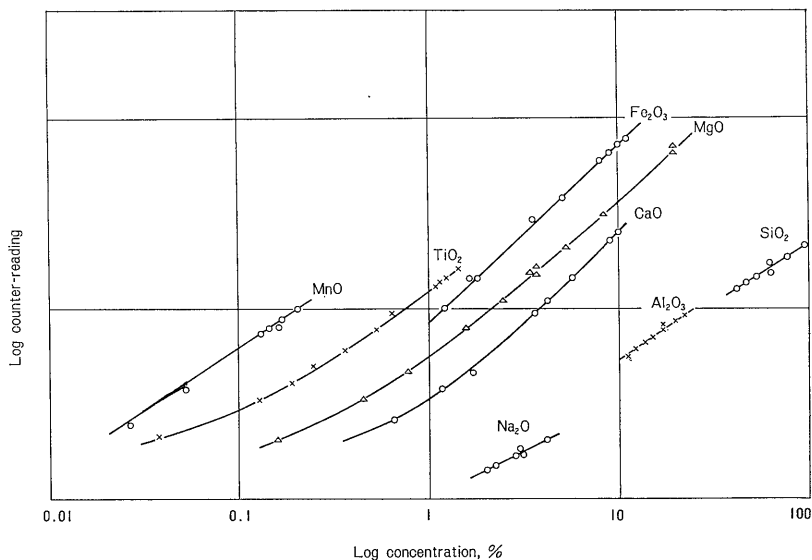


Fig. 6 Working curves for some major elements, by pellet-high voltage spark method. Standard pellets of known concentrations are prepared with geochemical reference samples: W-1, G-1, G-2, GSP-1, AGV-1, BCR-1, DTS-1, PCC-1, SY-1, JG-1, JB-1 (Flanagan, 1973).

and a hand mortar), and is sieved with a 200 mesh screen. An equal amount of (0.5 g) glass powder and a graphite powder for pellet are mixed with a Spex mixer mill using a tungsten carbide capsule for 5 minutes. A mixture is then pressed into a 1/2" diameter pellet at 80,000 lbs/inch<sup>2</sup> for 10 seconds. High voltage spark method is applied for the excitation (30 KV, 0.015  $\mu$ F, 0.9 mH, 2  $\Omega$ , Ir=4.0 A, 4 Brks/H.C. electrode gap 3 mm, exposure 20 sec. or I.S. counting control, sample pellet: upper electrode, sharpen end graphite rod: lower electrode). Good precisions of about 3% in the coefficient of variation were obtained for the determination of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, CaO, MgO, TiO<sub>2</sub> and Na<sub>2</sub>O using Co 4867 Å, Co 3453 Å and Sr 3380 Å as internal standard lines. Working curves for the rock components are shown in Fig. 6.

### 3.2 Minor element

Detection limits for the minor elements in D.C. arc method are presented in Table 1 (lower values in the concentration ranges), and some typical example of working curves in Fig. 7 (D.C. arc: 230 V, 8 A, electrode gap 3 mm, preburn 3 sec., exposure 60 sec.).

One disadvantage inherent in the photoelectric spectrometer is a difficulty in background estimation (THOMPSON and BANKSTON, 1969). After a exposure, the total dark current of photomultiplier tube and background signals from the D.C. arc excitation are integrated together with the spectral energy of analytical line. Integrated value of dark current and D.C. radiation signals reaches appreciable amount for prolonged exposure. Photomultiplier response is linear, however as well known the back ground radiation

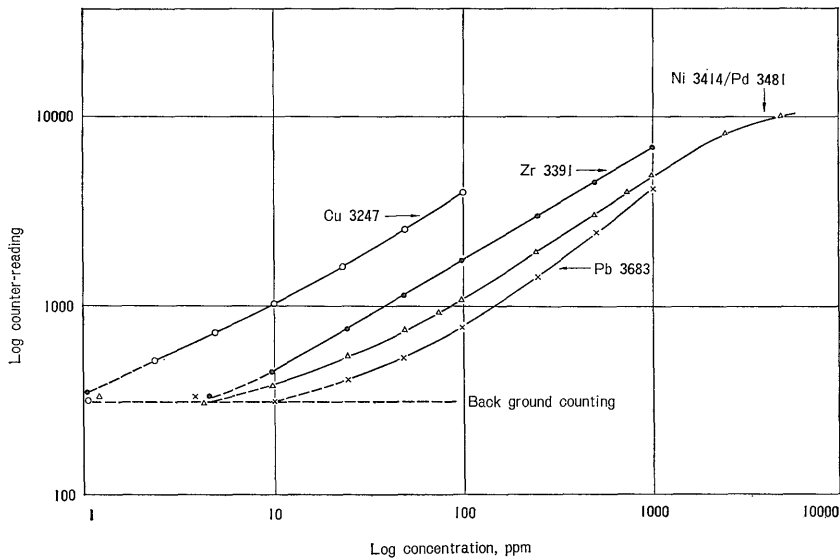


Fig. 7 Working curves for some minor elements, by powder D.C. arc method.  
Standard:  $\text{SiO}_2 + \text{NaCl}$  (1 + 1) base

of D.C. arc excitation is not stable hence the measurement and correction of background are necessary.

Background correction can be made by monitoring on the focal curve one or several positions which are free from the line and band interference. In the analytical programs B, C and D, if a complete lacking of an element is found in the samples, a photoelectric channel which is chosen for the element is usable for the background monitoring. D.C. arc background radiation for each photoelectric channel can be measured by arcing of blank samples which have the same major composition and the same buffer material. Two internal standard lines Pd 2658 Å and Pd 3481 Å can serve for the good background monitoring by conversion of an electric connection.

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## 地質試料分析用の GSJ・直読式発光分光分析装置について

安藤 厚・池田 喜代治

### 要 旨

地質試料を分析する目的でプログラムされた直読式発光分光分析装置 (ダイレクトリーダー) が地質調査所 (GSJ) に設置された。この装置の分析プログラム, 分析線, 光学系, 光電子増倍管の配置および発光源などの概要と, 地質試料分析への適用例をあげた。

#### 分析プログラム

- A) 珪酸塩主成分 10 元素 (Si, Al, Fe, Mn, Ca, Mg, Ti, P, Na, K)
- B) 珪酸塩微量成分 11 元素 (Ni, Co, Cr, V, Cu, Pb, Ba, Rb, B, Zr, Sr)
- C) 鉄・マンガン酸化物 18 元素 (Ni, Co, Fe, V, Cu, Pb, Ti, P, As, Zn, In, Mn, Cr, Sn, Si, Al, Mo, Mg)
- D) 硫化鉱 14 元素 (Ni, Co, Fe, Mn, Cu, Pb, Sb, Bi, As, Zn, In, Cd, Ag, Sn)

内部標準元素線として, 原子線 (Li 4972 Å, Co 4867 Å, Pd 3481 Å) およびイオン線 (Sr 3380 Å, Pd 2658 Å) 計 5 本を選択した。これらの内標線は上記の各分析プログラムと任意に組み合わせることができる。

装置は, パッシェン-ルンゲ方式, 1.5 m 凹面回折格子・直読式分光分析装置 (コンパクト・アトムカウンター, 日本ジャーレル・アッシュ社製)。波長範囲 2,000-8,000 Å, 分散度 5.45 (1 次) および 2.7 (2 次) Å/mm。分析希望元素の増大に伴い, 光電子増倍管の組み込み数は 40 本に達した。

発光源として, 高圧スパーク, マルチソース, 直流アークなど 6 種の励起回路がそなえられ, そのうち任意の回路が選択できる。

(受付: 1976 年 9 月 29 日; 受理: 1976 年 10 月 8 日)