NOTE

Identification of Barium Sulphates

Kazuo WADA, Samuro MIWA, Tokinobu KATO*

1 Introduction

There are three kinds of barium sulphate commercially. One is baryte. The second one is ground barium sulphate (ground baryte). Ground barium sulphate has two types, that is, water-ground barium sulphate and air-separated barium sulphate. They are manufactured by grinding baryte and washing with water or air-separating it to remove impurities. These two types of barium sulphate could be called natural barium sulphate. The last one is precipitated barium sulphate(synthetic barium sulphate),blanc fixe. It is chemically manufactured by precipitating barium sulphate from soluble barium salt solution. The starting material is usually baryte or witherite.

In the present Customs Tariff Schedules, it is necessary to identify these three kinds of barium sulphate. Besides barium sulphate, in Inorganic substance there are many compounds those require identification to classify them into Customs Tariff Schedules, whether it is mineral itself or having any physical and chemical processes. The examples are calcined magnesite and magnesium oxide, gypsum and calcium sulphate, natural corundum and artificial corundum, etc.

We previously reported[1)2)]on identification of magnesium oxides.

Many studies are reported on the structure of crystal of barium sulphate.[3)4)5)]and quantitative analytical methods of the elements containing in barium sulphate.[6)7)8)]But no paper has been reported on identification of barium sulphate. So the authors examined and discussed on it, especially on identification of ground barium sulphate and precipitated barium sulphate. Because they have similar physical and chemical properties.

2 Experimental

2．1 Samples

Samples employed for this examination are 19—baryte 11, ground barium sulphate 4,precipitated barium sulphate 4. The appearance, origin and supplier of the samples are listed in Table 1.

The lump sample of 11 kinds of baryte was powdered for following examination except for measurement of specific gravity. That is, the samples were crushed with agate mortar and pestle, then they were pulverized with Spex mixer mill No.8000 equipped a tungsten carbide capsule and balls.

In most cases, ground barium sulphate and precipitated barium sulphate were employed for the examination without any preparation.

2．2 Measurement of specific gravity

True specific gravity was measured on all samples without any preparation. That is, baryte was in lump form, the others were in powder form. But sample No.6 to 10 of baryte were measured in powder form, too. Beckman-Toshiba air comparison pycnometer, Model 930 was employed for the measurement.

Apparent specific gravity was measured only on ground barium sulphate and precipitated barium sulphate by applying JIS K 6220 method.[9)]

2．3 Qualitative analysis

Emission spectroscopy was employed.

Apparatus: Shimadzu plane grating spectrophotograph, Model GE340

Conditions: DC arc 5 amp.,600lines/㎜ grating, slit 20μ,2200～4600Å wave length, Kodak SA-1

*Central Customs Laboratory, Ministry of Finance,531,Iwase,Matsudo-shi,Chiba-ken,Japan

Table 1 Barium sulphates' samples used for the examination

Commodity name	Sample No.	Appearance	Produced country	Supplier	Remarks
Baryte	1	Lump	India	J.I.C.I.A.	
	2	〃	P. R. China	〃	J.I.C.I.A.
	3	〃	〃	Osaka Cust.	=Japan Inorganic
	4	〃	〃	〃	Chemicals Industry
	5	〃	〃	Tokyo Cust.	Association
	6	〃	Japan i)	N.C.Co.,	N.C.Co.,
	7	〃	〃 ii)	〃	=Nihon Chikagaku
	8	〃	〃 iii)	〃	Co., Ltd.
	9	〃	〃 iv)	〃	
	10	〃	R.Korea v)	〃	
	11	〃	U.S.A. vi)	〃	
Barium sulphate (ground)	12	Grey powder	Japan	J.I.C.I.A.	Origin (P.R. China)
	13	〃	〃	〃	
	14	〃	〃	〃	Origin (P.R. China)
	15	〃	〃	〃	
Barium sulphate (precipitated)	16	White powder	〃	〃	
	17	〃	〃	〃	Origin (P.R. China)
	18	〃	P.R.China	Osaka Cust.	
	19	〃	Japan	W.P.C.I.Co.,	W.P.C.I.Co., =Wako Pure Chemicals Industry Co., Ltd.

i) Hokkaido, Katsuyama Mine
ii) Akita-ken, Miyatamata Mine
iii) Kyoto-fu, Kasadori Mine
iv) Kyoto-fu, Funaoka Mine
v) Kinka, Nakagawa Shodo Mine
vi) Colorado, Stering Weld Co.

2. 4 Quantitative analysis

2. 4. 1 Barium sulphate

JIS K 5115 method was employed.

2. 4. 2 Strontium

Hydrochloric acid solution of sample was prepared by JIS K 5115 method above mentioned. The acid solution was submitted for determination of strontium applying atomic absorption spectrophotometry reported by Michalewska et al.

Apparatus and condition: Perking Elmer atomic absorption spectrophotometer, Model 303, wave length 460.73 nm.

2. 4. 3 Lead

Sample solution was prepared by the same procedure of 2.4.2(JIS K 5115 method). Lead content was determined by applying atomic-absorption spectrophotometry described in JIS K 0102,37.2(3), Note(2).

Apparatus and condition: The same as 2.4.2,wave length 217.0nm.

2．5 Scanning electron microscopic analysis

Four samples of ground barium sulphate and four precipitated barium sulphate were observed. Powder sample was dispersed in water or acetone by ultrasonic wave. A drop of the dispersed sample solution was put on adhesive tape fixed on a brass speciman holder. Then the sample was vacuum coated with carbon and gold.

Apparatus: JEOL scanning electron microscope, Model JSM-35

Conditions: Accelerating voltage 20 or 25kV,magnification 1,000 or 10,000

2．6 X-ray diffractiometry

2．6．1 Preparation of sample

In addition of powdered samples prepared in 2.1, some of ground barium sulphate and precipitated barium sulphate were pulverized into fine powder to pass 200, 250, 325 mesh of sieves with agate mortar and pestle.

2．6．2 Conditions

X-ray diffraction pattern was recorded by using Rigaku Denki Geiger-flex X-ray diffractometer, Model D-2, under the conditions in Table 2.

Table 2 Conditions of X-ray diffractiometry

Conditions	a	b	c
Target	Cu	Cu	Cu
Filter	Ni	Ni	Ni
Voltage (kV)	35	30	30
Current (mA)	20	20	20
Count full scale (cps)	4000 or 8000	2000 or 4000	2000* 4000 or 8000**
Time constant (sec.)	1	1	1
Scanning speed (/min.)	1/4	1	1/2
Chart speed (mm/min.)	2.5	20	20
Divergence slit ( )	1	1	1
Receiving slit (mm)	0.15	0.15	0.15
Detector	SC	SC	SC
Range 2 ( )	90 5	30 24	30 25

*Precipitated barium sulphate

**Ground barium sulphate

3 Results

3．1 Specific gravity

The results are shown in Table 3. There is not clear difference among of baryte, ground barium sulphate and precipitated barium sulphate in true specific gravity. Sample Nos.7 and

8(baryte) show rather low value. It is considered to be due to contain much impurity such as silicon, iron. But they show remarkable difference between ground barium sulphate and precipitated barium sulphate in apparent specific gravity.

Table 3 Specific gravity of barium sulphates

Commodity name	Sample No.	True S.G.	Commodity name	Sample No.	Tube S.G.	Apparent S.G.
Baryte	1	4.30	Barium sulphate (ground)	12	4.35	2.05
	2	4.42		13	4.36	1.79
	3	4.38		14	4.32	1.77
	4	4.40		15	4.39	1.94
	5	4.31	Barium sulphate (precipitated)	16	4.44	0.73
	6	4.44(4.45)		17	4.38	0.75
	7	3.60(3.94)		18	4.43	1.01
	8	3.67(3.75)		19	4.35	1.14
	9	4.36(4.55)				
	10	4.43(4.56)				
	11	4.02				

The value in( )shows the S.G. in powdered state.

3. 2 Qualitative analysis

Qualitative analytical results by emission spectroscopy are shown in Table 4.

Alkali earth metal, strontium and calcium other than barium are found rather remarkably in all samples. Magnesium and aluminium are also found in all samples. Baryte and ground barium sulphate tend to contain more lead, iron, copper, zinc and silicon as minor component than precipitated barium sulphate. For example silicon is fairly found in sample Nos.1, 4, 6, 8, 10, 11 of baryte and sample Nos.12 to 15 of ground barium sulphate, but it is scarcely found in precipitated barium sulphate, sample Nos.16 to 19.

3. 3 Quantitative analysis

Analytical results are shown in Table 5. Some of baryte, Nos.7 and 8,having low value of true specific gravity, contain smaller amount of barium sulphate than the others. But in other samples, there is not any remarkable difference in the contents of barium sulphate, even in precipitated barium sulphate which is chemically treated.

Strontium content does not also show any particular difference among of these three kinds of barium sulphate.

Lead is not contained in precipitated barium sulphate and some of baryte.

3. 4 Observation by scanning electron microscope

Photographs of each four samples of ground barium sulphate and precipitated barium sulphate are shown in Photo Nos.1 to 12.

The particle size of ground barium sulphate is much larger than that of precipitated barium sulphate, but ground barium sulphate sometimes contains very small particles. The range of particle size is wide and its shape is irregular. As shown in Photo No.1, it is remarkable that those particles are rather large and angular. When a large and angular particle is magnified to 10,000 magnifications (Photo Nos.3 to 6), the fracture of the particle and very small particles sticking on the particle are clearly observed.

On the other hand, precipitated barium sulphate is too small (less1) to observe each particle at 1,000 magnifications. It seems that the particles are aggregating each other (see Photo Nos.7 and 8). When it is observed at 10,000 magnifications (Photo Nos.9 to 12) it is possible to observe each particle. The particle size is about 0.3μ and the shape is rather round not to

Table 4 Results of qualitative analysis by emission spectrophotography*

Commodity name	Sample No.	Ba	Sr	Ca	Mg	Pb	Al	Fe	Cu	Zn	Si
Baryte	1	+++	++	+	++	tr	+	—	+	tr	++
	2	++++	++	+	+++	tr	+	+	+	—	+
	3	+++	+++	+	tr	+	tr	—	++	—	—
	4	+++	++	+	tr	+	tr	—	+	—	+
	5	+++	++	+	tr	—	tr	—	+	—	—
	6	+++	++	+	+	—	tr	—	+	—	+
	7	++	++	+	—	+++	tr	—	tr	+	—
	8	++	++	+	+	—	+	+	++	—	+
	9	+	++	+	—	—	+	+	+—	—	—
	10	+++	++	+	+	+	tr	tr	+	—	+
	11	+++	+++	+	+	+	tr	—	+	+	+
Ground barium sulphate	12	+++	+++	++	+++	++	+	+	++	+	+
	13	+++	+++	+	++	+	+	+	++	+	+
	14	+++	+++	++	++	+	+	+	+	+	+
	15	++++	++	+++	+++	++	+	+	++	+	+
Precipitated barium sulphate	16	+++	++	+	+	—	tr	—	—	—	—
	17	+++	+++	+	+	—	tr	—	—	—	—
	18	+++	+++	+	+	—	tr	tr	tr	—	—
	19	++	++	+	tr	—	tr	—	—	—	—

*The symbols marked in this column mean as follows:

++++ : Very large amount
+++ : Relatively large amount
++ : Small amount
+ : Very small amount
tr : Trace
— : Not detected.

be angular as that of ground barium sulphate.

3．5 X-ray Diffraction pattern

X-ray diffraction patterns recorded in all samples under the condition (a) are nearly same in *d* value as standard barium sulphate pattern, JCPDS No.24—20 and 24—1035.

Typical diffraction patterns are shown in Fig.1 and *d* value and relative intensity are shown in Table 6. Observing the patterns of all samples, they are grouped into two types. One is those of precipitated barium sulphate and another is those of baryte and ground barium sulphate.

The relative intensity of pattern peak of precipitated barium sulphate (sample Nos.16 to19) is very similar in standard barium sulphate pattern, JCPDS No.24—1035. While the relative intensity of pattern peak of barite (sample Nos.1 to 11) and ground barium sulphate (sample Nos.12 to 15) was inconsistent each other. But all the patterns of baryte and ground barium sulphate are characteristic in the very strong peak of face (021) at d =3.44Å.

Table 5 Results of quantitative analysis

Commodity name	Sample No.	BaSO (wt%)	Sr (wt%)	Pb (wt%)
Baryte	1	93.45	0.02	0.00
	2	97.53	0.40	0.00
	3	93.94	0.50	0.00
	4	95.64	0.42	0.01
	5	92.57	0.22	0.00
	6	92.10	0.33	0.00
	7	71.02	0.37	0.26
	8	68.78	0.05	0.00
	9	96.23	0.17	0.04
	10	95.12	1.01	0.01
	11	93.90	0.14	0.00
Ground barium sulphate	12	95.35	0.34	0.05
	13	93.70	0.30	0.03
	14	92.53	0.55	0.04
	15	92.93	0.30	0.04
Precipitated barium sulphate	16	96.56	0.04	0.00
	17	96.36	0.38	0.00
	18	95.49	0.98	0.00
	19	94.65	0.44	0.00

The absolute intensity at the peak of face (021) measured under condition (a), shows about 1,200～1,300 CPS in four samples of precipitated barium sulphate and about 1,700～3,500 CPS in ground barium sulphate. Absolute intensity of the peaks of crystal faces other than face (021) closely resemble in natural and synthetic barium sulphate.

Intensity ratio of face (121)/(021) in peak height and peak area are calculated. Because peak intensity of face (021) has remarkable difference between natural barium sulphate and synthetic one and the peak of face (121)(d =3.10Å) gives similar intensity through all samples and it appears neighbouring to the peak of face (021). The results are shown in Table 7.

Height ratio and area ratio of the peak are about 1.0 in all precipitated barium sulphate. But in natural barium sulphate, height ratio is 0.25 to 0.68 and area ratio is 0.25 to 0.85. The value is considerably different in origin. But the value is very small compared with precipitated barium sulphate. It was considered that the difference of relative intensity of pattern peak comes from the difference of particle size. So the patterns were recorded under the condition (c) on samples that were pulverized to pass sieves of 200, 250 and 325 mesh in four samples of ground barium sulphate and four samples of precipitated barium sulphate. And the ratio of face (121)/(021) was calculated. The results are shown in Table 8. The value is not so different in the value of Table 6. It means that the characteristic difference of relative intensity of X-ray diffraction pattern peak does not come from the difference of particle size.

4 Discussion

The value of the specific gravity does not show any difference in all samples except sample Nos.7 and 8. The value is not helpful to identify baryte, ground barium sulphate and precipitated barium sulphate.

Apparent specific gravity of precipitated barium sulphate is smaller than ground barium sulphate. But it is difficult where to make a demarcation line to identify them between 1.0 and 2.0 of apparent specific gravity. From qualitative analytical results, it is only said that if the elements other than alkali earth metal are detected, it is possible to be baryte or ground barium sulphate. But there is a case that some of baryte contain only very small amount of impurities. So it is difficult to identify them by only qualitative analysis.

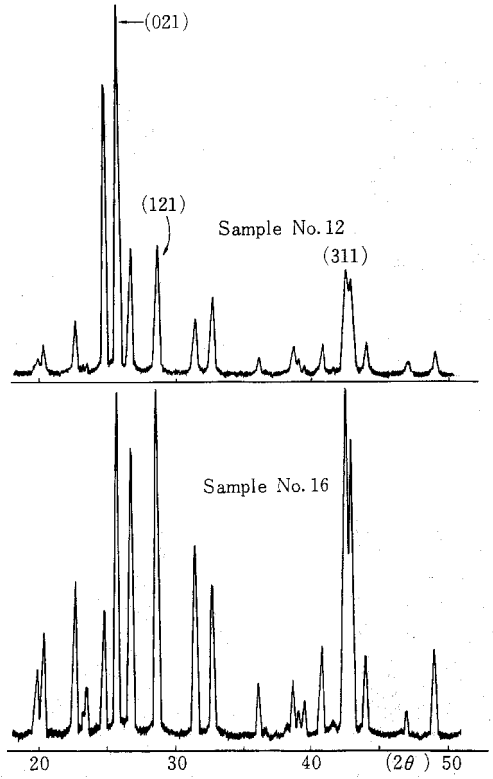

Fig.1 X-ray diffraction patterns of barium sulphate

Observation by scanning electron microscope is reliable method to identify barium sulphates.

Particle size of precipitated barium sulphate is greatly effected with concentration of barium ion in the solution, when it is manufactured. This is satisfactorily understood by von Weimarn's equation concerning reaction rate of precipitate formation of slightly soluble salts.

$$V = K\,\frac{Q-S}{S}$$

Where V : reaction rate of precipitate formation
Q : concentration of supersaturated solution just before precipitation
S : solubility of precipitate
K : constant

The concentration Q is usually taken in large value in preparation of precipitated barium sulphate in industrial manufacturing. Accordingly, the value V becomes large. From this reason, it is understood that a lot of nucleus of precipitate is formed and the particle size of the precipitate is getting small. Takiyama's experiment also proved the phenomenon. Precipitated barium sulphate is usually used for pigment. Ground barium sulphate is not used for pigment but is mainly used for oil-well treatment. So, it does not need to be fine particle. It is usually several tens microns.

Consequently most of commercial barium sulphate is possible to identify by scanning electron microscope.

In X-ray diffractiometry, the characteristic difference is found between X-ray diffraction pattern of crystal of natural barium sulphate and synthetic barium sulphate. It suggests that powder X-ray diffractiometry is a effectual method for identification of them. It's necessary to make clear the cause of characteristic difference of relative intensity pattern. But it is not made this examination.

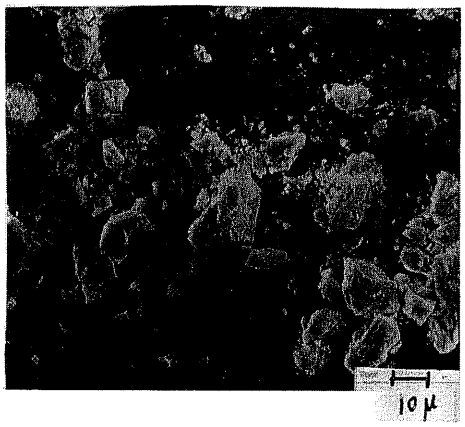

Photo 1 Ground barium sulphate No.12(×1,000)

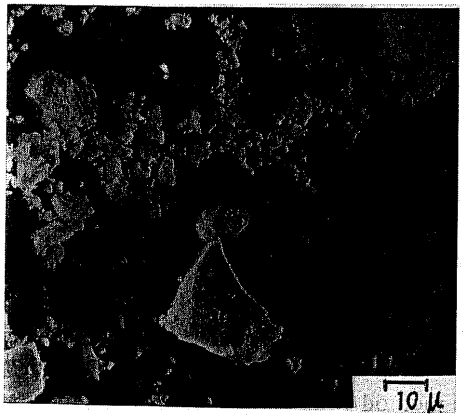

Photo 2 Ground barium sulphate No.15(×1,000)

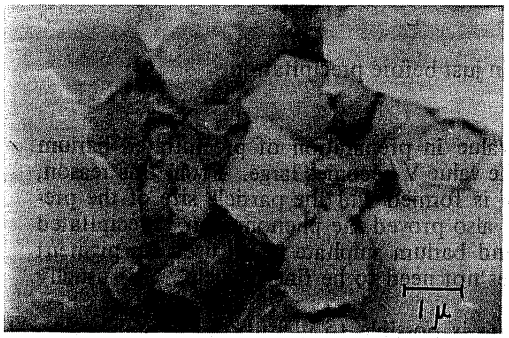

Photo 3 Ground barium sulphate No.12(×10,000)

Photo 4 Ground barium sulphate No.13(×10,000)

Photo 5 Ground barium sulphate No.14(×10,000)

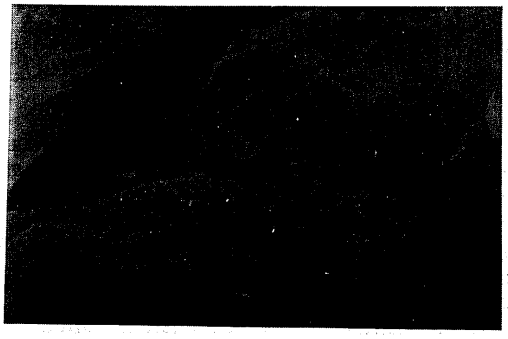

Photo 6 Ground barium sulphate No.15 (×10,000)

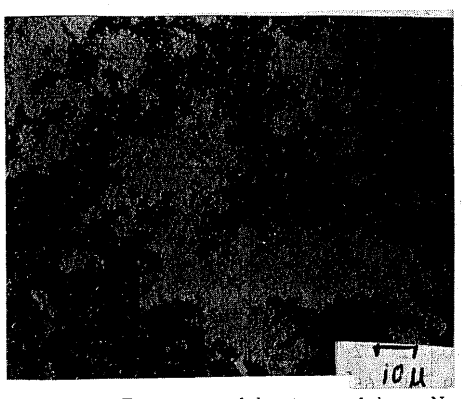

Photo 7 Precipitated barium sulphate No.17
(×1,000)

Photo 10 Precipitated barium sulphate No.17
(×10,000)

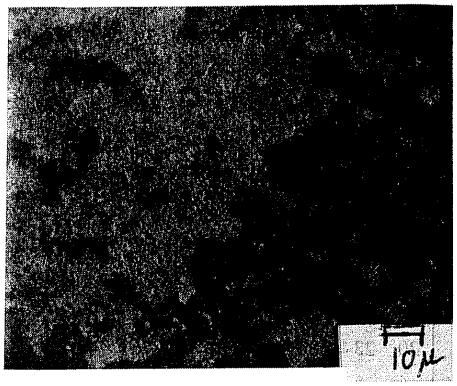

Photo 8 Precipitated barium sulphate No.18
(×1,000)

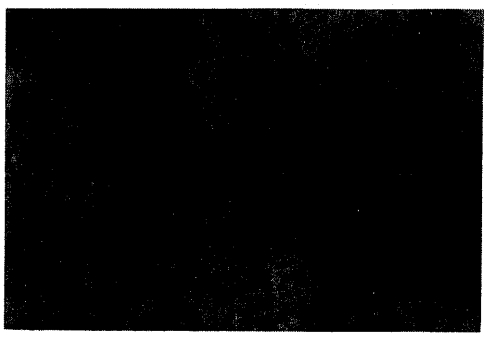

Photo 11 Precipitated barium sulphate No.18
(×10,000)

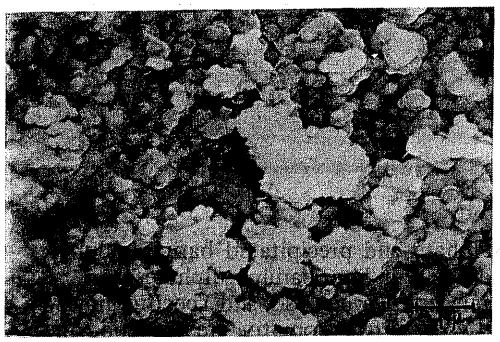

Photo 9 Precipitated barium sulphate No.16
(×10,000)

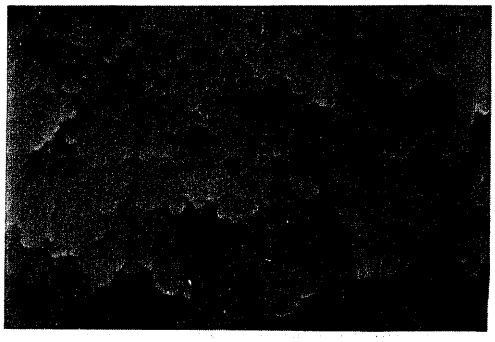

Photo 12 Precipitated barium sulphate No.19
(×10,000)

Table 6 *d* Value and relative intensity of X-ray diffraction pattern ($2\theta = 20 \sim 50°$) of barium sulphates

d value (A)	Face (hkl) \ Sample (No.)	Relative intensity (I/I)																			
		Baryte											Ground barium sulphate				Precipitated barium sulphate				
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	*
4.44	020	7	8	7	5	5	6	10	11	8	6	15	5	5	4	5	18	22	20	15	16
4.33	101	12	13	11	8	8	10	15	19	12	10	22	9	11	9	10	30	30	28	30	30
3.89	111	20	20	18	13	12	16	22	28	20	15	35	14	18	15	15	46	44	45	47	50
3.77	120	4	4	4	3	2	4	5	7	5	3	10	2	2	2	3	13	14	14	11	12
3.57	200	56	58	52	56	45	56	47	39	48	51	39	68	65	86	64	34	35	30	29	30
3.44	021	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	98	99	100	100	100
3.31	210	41	38	35	23	22	29	43	51	39	29	64	34	33	30	35	77	80	73	68	70
3.10	121	43	49	44	33	31	38	52	58	47	35	73	34	41	34	36	100	100	98	99	95
2.83	211	21	19	17	13	14	15	21	24	20	15	32	16	18	15	16	53	53	51	51	50
2.73	130																				15
2.72	002	19	24	20	17	18	19	25	29	23	17	32	15	20	17	16	46	47	46	49	45
2.48	221	5	5	5	4	4	4	7	7	5	4	8	4	5	4	5	14	16	14	14	13
2.44	112, 131	<1	1	1	<1	<1	1	1	6	1	1	2	1	<1	1	1	3	4	2	3	2
2.32	022	7	8	7	6	7	6	8	9	8	6	12	7	7	7	6	14	15	14	15	14
2.30	310	4	4	3	2	3	3	5	6	4	3	8	4	3	3	4	6	8	7	6	6
2.28	230	3	3	3	2	2	2	5	7	4	2	7	2	2	2	2	9	10	8	8	8
2.21	122	10	11	10	7	9	8	11	15	11	8	16	8	9	9	8	26	27	26	26	25
2.16	202	2	1	1	<1	<1	1	1	<1	<1	1	1	1	1	1	<1	4	5	2	3	3
2.12	311, 140	31	34	29	21	23	26	43	51	38	27	69	26	27	22	26	83	84	81	78	80
2.10	212, 231	30	30	28	20	22	24		44	36	26		20	23	20	24	77	79	76	74	75
2.05	041	10	9	8	7	7	8	9	11	11	8	16	6	8	8	8	23	24	21	21	19
1.94	222	<1	<1	1	1	<1	<1	<1	<1	1	1	1	1	<1	<1	<1	2	3	1	2	1
1.93	132	3	3	3	2	3	3	3	4	3	3	6	3	3	2	3	7	8	7	8	7
1.85	330	7	5	5	4	4	6	7	7	5	5	11	5	5	5	5	20	20	19	19	18

*JCPDS card No.24—1035

5 Conclusion

Baryte is usually in lump form. Ground barium sulphate and precipitated barium sulphate are both in powder form. So the indentification is only necessary in later barium sulphates.

It is difficult to identify them by qualitative and quantitative analysis and specific gravity.

It is found that scanning electron microscopy and X-ray diffractiometry are the good methods to identify them.

Observing particle of ground barium sulphate with scanning electron microscope, it is irregular and angular. But in precipitated barium sulphate, it is smaller than ground barium sulphate, and generally round.

In X-ray diffraction pattern, there is a significant difference between natural barium sulphate and synthetic barium sulphate. Especially the peak intensity in d=3.44 Å of face(210)is very strong in natural barium sulphate.

Table 7 Peak intensity of face (121)/(021)*

Connodity name	Sample No.	Intensity ratio	
		Peak heigth	Peak area
Baryte	1	0.43	0.50
	2	0.32	0.40
	3	0.33	0.32
	4	0.32	0.29
	5	0.30	0.39
	6	0.28	0.37
	7	0.50	0.63
	8	0.59	0.73
	9	0.47	0.60
	10	0.36	0.47
	11	0.68	0.85
	Av.	0.42	0.50
Ground barium sulphate	12	0.29	0.38
	13	0.25	0.32
	14	0.34	0.42
	15	0.30	0.30
	Av.	0.30	0.36
Precipitated barium sulphate	16	1.06	1.04
	17	1.02	1.01
	18	1.01	1.03
	19	0.99	1.03
	Av.	1.02	1.03

*Recorded under the condition b

Table 8 Peak intensity of face (121)/(021)

Connodity name	Sample No.	Particle size	Intensity ratioo	
			Peak height	Peak area
Ground barium sulphate	12	under 200 mesh	0.290	0.360
		〃 250 〃	0.302	0.360
		〃 325 〃	0.298	0.362
	13	〃 200 〃	0.334	0.392
		〃 250 〃	0.312	0.366
		〃 325 〃	0.258	0.312
	14	〃 200 〃	0.280	0.338
		〃 250 〃	0.318	0.378
		〃 325 〃	0.344	0.394
	15	〃 200 〃	0.282	0.360
		〃 250 〃	0.268	0.356
		〃 325 〃	0.298	0.374
Precipitated barium sulphate	16	〃 200 〃	1.026	1.053
		〃 259 〃	1.014	1.026
		〃 325 〃	0.968	1.008
	17	〃 200 〃	1.026	1.038
		〃 250 〃	1.024	1.050
		〃 325 〃	0.980	0.128
	18	〃 200 〃	1.002	1.058
		〃 250 〃	0.994	1.024
		〃 325 〃	0.926	0.960
	19	〃 200 〃	1.002	1.052
		〃 250 〃	1.034	1.043
		〃 325 〃	1.012	1.027

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