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Geoscience Laboratory, Geological Survey of Pakistan  
Islamabad

Volume 10 Special Issue  
August, 1995

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**Recommended Methods of  
Chemical Analysis for  
Geological Samples**

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Special Issue Editors

*Abdul Aziz*  
*Shiro Itoh*



Geoscience Laboratory Project  
Technical Cooperation between  
Geological Survey of Pakistan and  
Japan International Cooperation Agency



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## EDITORS' NOTE

This is the first special volume of the Geoscience Colloquium devoted exclusively on analytical geochemistry. It basically addresses the issues related to and the progress achieved in relation to the GeoLab's on-going research on the preparation of geological Standard Reference Materials (SRMs). It describes and recommends procedures for their accurate and dependable chemical analysis.

Identification and selection of suitable methods of analysis of different rocks, minerals and ores have always been of great importance not only for the analytical precision but also for drawing comparison between the available techniques, procedures and instrumentation. This volume contains some recommended procedures for analyzing silicate rocks, carbonates, chromite and phosphorite thus covering an appreciable range of methods applicable on most types of geological samples in Pakistan. Besides, the analytical procedures for such problematic and volatile elements like mercury, arsenic and antimony are also presented. These elements are often analyzed in connection with gold exploration and are also becoming increasingly important in various kinds of environmental and geomedical studies.

While describing different methods and techniques of analysis, strong emphasis has been placed on proper sample preparation as any error on this account will have compound effect on the accuracy of the results

The research data and information presented in this volume are partly tentative as some of these are being further improved, refined and upgraded through additional tests and experimentation. Their final versions will start appearing after mid 1996 in the future issues of the GeoLab's research publications. Meanwhile, the editors would very much welcome queries, comments, suggestion and criticism from co-researchers and the geanalysts working in and outside the Geological Survey of Pakistan.

Abdul Aziz  
&  
Shiro Itoh  
*Editors*





## ARTICLES



## **Geological Reference Samples Prepared for Analysis**

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### **INTRODUCTION**

It is to be noticed that the chemical analysis of a sample depends mainly upon the analytical method, instrument and the standards used. Furthermore, geological standard reference material (SRM) is essentially used to check the instrument and analytical techniques adopted for the analysis of geological samples. Some certified standard materials are available from various international institutes but usually of a very high cost.

Recent development of instrumental analysis for geological samples is greatly indebted to provide suitable standard materials for the analysis of trace elements. There are many kinds of standards like standards of weights and measures or industrial products, similarly the SRMs as far as chemical laboratory is concerned are the materials known for their chemical composition. Using the SRMs in instrumental analysis the accuracy has been improved, specially for the analysis of silicate rock samples and ore minerals. Moreover, the limits of detection for some rare metals have also been lowered.

Laboratories of geological research institutes have used the SRMs for the purposes (i) to compare the analytical accuracy among different laboratories, (ii) to develop new analytical methods, (iii) to produce the calibration curves for target elements, and (iv) to control the quality of chemical analysis. For these purposes, SRM generally requires extreme homogeneity, enough quantity and fine grain size.

Considering the importance of the availability of standard reference materials, the Geoscience Laboratory has undertaken a project to provide various standards of the rocks and minerals found in Pakistan. PG-1 (granite) is the first of such Geological Standard Reference Samples and it is followed by PGN-1 (gabbro norite), PPh-1 (phosphorite), PCr-1 (chromite), PBx-1 (bauxite), PGy-1 (gypsum), PSI-1 (slate), PMg-1 (magnesite), PLs-1 (limestone) and PDo-1 (dolomite).

Analytical studies have been conducted on these standard samples in collaboration with International Laboratories. For the first standard sample of Pakistan, PG-1, various latest and sophisticated techniques including wet chemistry, AAS unit, WD-XRF, ICP-AES, ICP-MS and INAA have been applied. However, the successively prepared standard samples are still on the way to accumulate precise analytical data for obtaining the certified values of chemical composition. Therefore, some of the results shown in this report may be revised according to the results of future analytical work.

The issuance of the standard samples is possible in Pakistan now, and its use in chemical analysis eradicates any discrepancies or errors. To obtain an accurate

analytical data, the utilization of Pakistan's Standard Reference Materials is thus strongly recommended.

### LOCALITIES OF STANDARD SAMPLES

Sample processing is initiated by the selection of rock (or mineral) types to be prepared. The type of rock (or mineral) is desired to be of the similar major compositions as that of the samples which are to be analyzed using the rock (or mineral) as a standard. The selection of sampling localities is, therefore, made through careful observations on fresh outcrops of the rock (or mineral) type. The location being weathered should not be sampled as large quantity of water in the weathered sample is undesirable for SRM.

The localities of the standard samples are briefly summarized in Table 1.

Table 1. Location of Pakistan's Standard Samples

SRM	Rock or mineral type	Locality
PG-1	granite	quarry along main road side, Malakand, NWFP
PGN-1	gabbro norite	outcrop along Karakoram Highway, Chilas, N. Pak.
PPh-1	phosphorite	outcrop in Kakul mining area, Abbottabad, NWFP
PCr-1	chromite	ore from Heroshah mine, Malakand, NWFP
PBx-1	bauxite	outcrop in Salt Range region, Punjab
PBa-1	barite	outcrop in Duddar mining area, Balochistan
PGy-1	gypsum	outcrop in Khewra Gorge-Salt Range, Punjab
PMg-1	magnesite	quarry in Kumhar mining area, Abbottabad, NWFP
PDo-1	dolomite	quarry in Kumhar mining area, Abbottabad, NWFP
PLs-1	limestone	quarry in Margalla Hill, along GT road, Punjab
PSl-1	slate	outcrop in Attock Slate, Nowshera, NWFP

### PREPARATION OF STANDARD REFERENCE SAMPLE

The samples brought back to the laboratory are crushed with a jaw crusher and further pulverized to minus 140 mesh with a ball mill. The pulverized sample is then mixed well through quartering process. Four mounds of the quartered sample powder are usually piled up into a mound, which is again quartered. The process is repeated until the sample powder proves homogeneous. To test the homogeneity, XRF, ICP and some other efficient analytical technique are applied for a quick analysis of some major elements in several subsamples, randomly taken out of a whole sample mound. After the homogeneity is proven, bottling of the sample is carried out.

Putting about 40 g of the homogenized powder into each bottle leads to produce some 1,000 bottles of the standard from a 40 kg rock sample. When the samples are bottled from different piles, each bottle is labeled and numbered bearing a combination of pile number and serial number for the user's reference and record.

## ANALYTICAL RESULTS OF STANDARD SAMPLES

The Pakistan's SRMs are analyzed in collaboration with International Laboratories. Wet chemistry, AAS, XRF, ICP-AES, ICP-MS and INAA have been applied for this purpose. An average chemical composition for each standard reference sample is shown in Table 2 for major elements and Table 3 for trace elements.

Table 2 Average chemical composition of Pakistan's Standard Reference Samples for major elements (in %) "-" means "not determined yet".

Element	PG-1	PGN-1	PPh-1	PCr-1	PLs-1	PDo-1	PMg-1
SiO <sub>2</sub>	73.93	50.04	2.64	14.58	0.84	3.21	1.48
TiO <sub>2</sub>	0.12	1.60	0.01	0.16	0.00	0.00	0.00
Al <sub>2</sub> O <sub>3</sub>	14.52	16.94	0.24	10.52	0.19	0.11	0.11
Fe <sub>2</sub> O <sub>3</sub>	0.25	3.18	0.33	-	0.05	0.44	0.45
FeO	0.27	8.45	-	11.91	-	-	-
MnO	0.01	0.19	0.01	0.13	0.04	0.42	0.04
MgO	0.15	5.50	0.11	26.03	0.94	20.12	46.13
CaO	1.04	9.79	52.85	0.11	53.83	29.92	0.58
Na <sub>2</sub> O	4.60	3.33	0.29	0.01	0.04	0.03	0.03
K <sub>2</sub> O	5.47	0.25	0.06	0.01	0.01	0.04	0.01
P <sub>2</sub> O <sub>5</sub>	0.03	0.26	37.22	0.06	0.00	0.09	0.02
H <sub>2</sub> O <sup>+</sup>	0.35	0.05	0.47	0.71	0.26	0.15	0.09
H <sub>2</sub> O <sup>-</sup>	0.14	0.08	0.22	1.40	0.10	0.01	0.05
F	-	-	3.54	-	-	-	-
SO <sub>3</sub>	-	-	0.37	-	-	-	-
CO <sub>2</sub>	-	-	1.43	0.94	43.27	45.45	50.83
Cr <sub>2</sub> O <sub>3</sub>	-	-	-	33.42	-	-	-
Cl	-	-	0.01	-	-	-	-
Total	100.87	99.66	99.80	99.99	99.57	99.99	99.82
LOI	-	-	-	-	43.68	45.62	50.97

Table 3. Average chemical composition of Pakistan's Standard Reference Samples for trace elements (in ppm) "-" means "not determined yet".

Elem.	PG-1	PGN-1	Elem.	PG-1	PGN-1	Elem.	PG-1	PGN-1
As	339	-	Gd	3	3	S	39	-
Ba	1026	77	Hf	3	-	Sb	0.21	0.03
Ce	32	18	Ho	0.25	0.69	Sc	0.75	35
Co	3	38	La	15	8	Sm	4	3
Cr	2	65	Lu	0.08	0.27	Sr	683	390
Cs	7	0.03	Mo	0.8	-	Th	12	0.16
Cu	2	140	Nb	17	13	U	3.58	0.05
Dy	2	4	Ni	5	52	V	8	440
Eu	1.05	1.15	Pb	61	3	Yb	0.57	2.05
F	580	-	Pr	4	3	Zn	43	115
Ga	21	-	Rb	173	1	Zr	136	-

## Decomposition of Geological Samples

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### INTRODUCTION

Decomposition of samples is the first step after pulverization in the analytical procedures using AAS or ICP-AES for geological materials. Considering the objective of the analysis, it is necessary to choose the sample decomposition technique. There is no single decomposition technique capable of dissolving all elements in all types of geological samples. In reality, decomposition technique should be chosen under the consideration of and to be consistent with the chemical and mineralogical characteristics of the samples, elements to be analyzed, precision and accuracy desired, instruments, laboratory facilities available, and time available for analysis.

The development and application of modern analytical instrumentation has provided rapid and sensitive methods for multi-element geochemical analysis. Accordingly, conventional sample decomposition techniques by acid digestion, fusion with fluxes, or others which require laborious procedures, cannot keep pace with the productivity of the modern instruments. Full research efforts, therefore, should be devoted to creating a streamline of sample decomposition techniques so that productivity of sample decomposition and element determinations may become at equal pace in geological analysis.

The authors referred Chao and Sanzalone (1992)<sup>1</sup> to all of the chapter below.

### DECOMPOSITION BY ACID DIGESTION.

Acid digestion is a convenient way to decompose geological samples for analysis. It is flexible in the type of acid mixtures to be used, choice of either open or closed digestion system, and time and temperature of heating. In the case of acids digestion, the resultant sample solution is not added with extraneous salts which are often troublesome in trace element determinations because they may cause matrix interferences and clogging of the transport system of spectrometric methods.

#### Type of acids

##### (a) Hydrofluoric acid (HF)

Hydrofluoric acid is a weak non-oxidizing inorganic acid and the most effective mineral acid for breaking up the strong Si-O bond, forming  $\text{SiF}_4$  which volatilizes upon heating. The disintegration of the silicate lattice leads to the liberation of metals bound within the silicate structure. However, As, B, Ti, Nb, Ta, Ge and Sb are totally or partially lost through volatilization as fluorides. Although HF has shown to be able to work effectively by itself, it is generally used with other acids. The mixture of acids increases the capability of HF in decomposing the accompanying non-silicate rock

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<sup>1</sup> Chao and Sanzalone (1992), J. Geoch. Expl., vol. 47

minerals (e.g. sulfides and oxides) and to moderate the initial strong reaction of HIF alone.

**(b) Hydrochloric acid (HCl)**

Hydrochloric acid is the most frequently used acid for dissolution of geologic samples. It dissolves carbonates, phosphate, borate and sulfate except barite. It solubilizes some sulfides, but its action on pyrite is limited. When HCl is combined with an oxidant such as  $\text{KClO}_4$  or  $\text{H}_2\text{O}_2$ , its effectiveness is significantly increased so that many sulfide minerals can be decomposed and brought into solution. It is the preferred acid medium to dissolve residues after acid digestion or melts of alkali fusion for later analysis by AAS.

**(c) Hydrobromic acid (HBr)**

Hydrobromic acid is less commonly used than HCl for sample decomposition. The effectiveness of HBr as a decomposition agent is enhanced by the presence of an oxidant such as NaBr or concentrated  $\text{HNO}_3$ . The effects of the HBr-oxidant mixture are similar to those of aqua regia. HBr in combination with free bromine ( $\text{Br}_2$ ) has been employed to extract Au, Pt, Pd and Te from geological samples.

**(d) Nitric acid ( $\text{HNO}_3$ )**

Hot and concentrated  $\text{HNO}_3$  is a strong oxidizing acid and commonly used to decompose sulfides, selenides, tellurides, arsenides and sulfoarsenides. The mixture of concentrated  $\text{HNO}_3$  and concentrated HCl in a volume ratio of 1 : 3 is aqua regia and has a much stronger oxidizing and dissolving power than  $\text{HNO}_3$  alone.

Aqua regia should be used when freshly prepared because on standing it loses its strength. There is no such reagent as 'dilute' aqua regia. Aqua regia attacks Au, Pt, and Pd. It also decomposes sulfides including pyrite, arsenides, selenides and some Mo and W minerals. The strength of aqua regia can be enhanced by adding free bromine.

**(e) Perchloric acid ( $\text{HClO}_4$ )**

Perchloric acid has powerful oxidizing and dehydrating properties when it is concentrated and hot. It loses its oxidizing power upon dilution with water. Because of its high boiling point (203 °C), it is used to drive off HF and other more volatile acids by fuming. The perchlorates formed after decomposition with  $\text{HClO}_4$  are readily soluble in water. Perchloric acid is most often used with other acids, especially HIF. Anhydrous salts of  $\text{HClO}_4$  may cause spontaneous burning and also explosion in the presence of organic materials. Therefore, evaporation involving  $\text{HClO}_4$  must be carried out in a hood specially designed for this purpose with wash down facilities for cleaning after use.

**(f) Sulfuric acid ( $\text{H}_2\text{SO}_4$ )**

Sulfuric acid has dehydrating and mild oxidizing properties when it is hot. Sulfuric acid alone or in combination with other acids has not been applied widely in the decomposition of geological samples. It is because of the low solubility of alkaline earth and Pb sulfates, and depressing effect of sulfate on the signal of alkaline earth metals when determined by AAS. However, hot concentrated  $\text{H}_2\text{SO}_4$  has special uses like breaking up monazite, sulfides of As, Sb, Se and Te, and Nd and Ta minerals in the presence of  $(\text{NH}_4)_2\text{SO}_4$ . Fluorspar can also be decomposed by evaporation with  $\text{H}_2\text{SO}_4$ .

### (g) Phosphoric acid ( $H_3PO_4$ )

Phosphoric acid has high boiling point and low volatility. As phosphate ions can cause interferences by complexing or precipitating some of the elements to be determined,  $H_3PO_4$  is not yet used frequently in silicate analysis. However, it is particularly effective to decompose chromite for the determination of Cr and associated metals

The potential of  $H_3PO_4$  as an acid decomposition agent has not been fully explored. With improved analytical instrumentation, sensitivity of determination has been increased and interferences have drastically been reduced so greater use of  $H_3PO_4$  in sample decomposition should be considered.

## ACID DECOMPOSITION IN AN OPEN SYSTEM

When a geological sample is heated above room temperature with HIF in combination with other mineral acids in an open vessel, Si and F are volatilized as  $SiF_4$ . The obtained sample solution has some advantages, from the analytical point of view, such that the salt content of the solution is reduced for the benefit of elemental determination by AAS and ICP-AES. Complete removal of fluoride from sample solution is not always straight-forward and is often difficult to accomplish. If not removed, fluoride may form insoluble precipitates and tie up some analytes leading to negative errors in the analysis. On the other hand, if elements associated with the insoluble fluoride are of no interest for the overall analysis of given samples, such precipitates may be ignored. Fluoride can be removed by heating with a high-boiling mineral acid such as  $HClO_4$  and  $H_2SO_4$ .

Sample decomposition involving HIF in an open vessel is a convenient method to dissolve silicate rocks for large batches of samples. However, one should be aware that some refractory minerals are incompletely decomposed and some elements are lost by volatilization. The petrological and mineralogical nature of the sample as well as elements to be determined should be considered when choosing this method for decomposition, and alternate procedures such as acid attack in a closed system or fusion with alkali fluxes should be adopted.

## ACID DECOMPOSITION IN A CLOSED SYSTEM

Decomposition of geological materials with acid mixtures containing HIF in a closed system is more efficient than in an open system. This is related to the increased reactivity of the acids at high temperatures and pressures. Advantages of this method include the retention of volatile elements such as As, Be, Cd, Cr, Hg, Pb and Se. Various types of vessels are available for use in sample decomposition in a closed system. Among them PTFE (polytetrafluoroethylene) crucibles sealed in steel or aluminum casing and all Teflon vessels with thick wall but no metal casing are in common use. The different vessels have different temperature limits. PTFE-lined pressure vessels can withstand temperature in the range of 150 to 250 °C. Decomposition at room to boiling-water temperatures can be conveniently carried out in tightly capped polypropylene, polycarbonate, or Teflon vessels without the outer metal casing. The time of reaction within the closed vessel varies from 30 minutes to several hours depending on the temperature chosen and the type of sample to be decomposed. Lower temperature may be compensated by prolonging the reaction



time. Silicate rocks have been digested with aqua regia + HF in all Teflon sealed vessels at 25 °C for 36 hours for the determination of heavy metals by AAS.

The PTFE-lined vessel is not designed to be used routinely for many samples because of the high cost of the vessel. It is, however, very useful when complete dissolution is required for selected refractory samples. For routine work, relatively inexpensive screwcapped Teflon bottles of 15 ml capacity or larger have been used. These can be conveniently used at room temperature or on a steambath. The general practice is to allow the sample and decomposition mixture to remain overnight in the bottle and to finish the digestion the next day. Occasionally, precipitates may be formed at the bottom of the vessel. However, if the precipitate do not contain the elements to be determined, no further treatment is necessary. This can speed up the sample decomposition considerably.

### DECOMPOSITION BY FUSION

The greater efficiency of decomposition by fusion as compared to acid digestion is mainly due to the high temperature used for fusion (500 ~ 1000 °C) These temperatures cannot be obtained in acid digestion owing to the boiling points of the respective acids.

However, decomposition by fusion has some disadvantages such as:

- (a) Samples cannot be analyzed for elements that comprise the flux (e.g. Li, B, Na, K and S).
- (b) Some contaminants originated in the flux are also brought into the sample solution.
- (c) High salt concentrations in the final solution often cause matrix problems as blockage of nebulization, spectral interferences and so on.
- (d) Large numbers of samples are more difficult to be decomposed by fusion in a streamline than by acid digestion.

It is often desirable even necessary to use fusion for the decomposition of refractory minerals that resist acid attack. Fusion has also been employed to decompose insoluble residues left by acid digestion where complete dissolution of the sample is required.

### TYPE OF FLUXES

#### (a) Sodium carbonate and sodium hydroxide ( $\text{Na}_2\text{CO}_3$ , $\text{NaOH}$ )

By these fluxes, the elements of samples are converted to soluble silicates and aluminates or to precipitates which are more easily dissolved by acid than the original mineral forms. The oxidizing ability of  $\text{Na}_2\text{CO}_3$  and  $\text{NaOH}$  can be enhanced by including  $\text{KNO}_3$  or  $\text{NaNO}_3$  to carry out the decomposition of sulfide and reducing materials. The alkali fusion with the carbonate and hydroxide has been replaced recently by fusion with lithium borate or acid digestion, especially for the determination of trace elements. This is probably because of impurities in the carbonate fluxes. Nevertheless, alkali fusion is commonly used to decompose geological samples for the determination of fluoride, and for the elements such as B, Mo, V and W using  $\text{K}_2\text{CO}_3$ - $\text{KNO}_3$  and  $\text{Na}_2\text{CO}_3$ - $\text{NaNO}_3$  as fluxes.

#### (b) Lithium metaborate and tetraborate ( $\text{LiBO}_2$ , $\text{Li}_2\text{B}_4\text{O}_7$ )

These are non-oxidizing fluxes that have been utilized for decomposition of geological materials. Even the refractory minerals (chromite, ilmenite, etc.) are readily

decomposed. The metaborate is much more active than the tetraborate as a fluxing agent. The difference between  $\text{LiBO}_2$  and  $\text{Li}_2\text{B}_4\text{O}_7$  lies in the higher acidity (higher content of  $\text{B}_2\text{O}_3$ ) of the latter. Thus, the metaborate is a better flux for acidic rock (high silica) and tetraborate is better for basic rock (low silica). A 2+1 mixture of  $\text{Li}_2\text{B}_4\text{O}_7$  and  $\text{Li}_2\text{SO}_4$  has been found to be exceptionally effective for the rapid decomposition and dissolution of silicate rocks. One g of the mixture will decompose 0.1 g of silicate rock at 1000 °C in a Pt crucible in 10 - 15 minutes or less, and the cooled melt can be completely dissolved by 20 mL of 1.2 M HCl at 90 - 100 °C in 5 minutes

#### (c) Sodium peroxide ( $\text{Na}_2\text{O}_2$ )

Sodium peroxide is a very powerful oxidization alkali flux in rock analysis. It releases oxygen at temperatures above its melting point (~ 480 °C). Many refractory minerals are effectively decomposed by heating with  $\text{Na}_2\text{O}_2$  at a temperature below 500 °C. These minerals include among others, chromite, zircon, rutile, ilmenite, bauxite, beryl, titanite and cassiterotantalite. The time of fusion required for the above minerals ranges from a few minutes to 20 minutes. A peroxide fusion is also effective for the decomposition of sulfides, arsenides, rare earth phosphates, W, Nb and Ta minerals, zirconium oxides and vanadates. The flux to sample ratio in sample decomposition by fusion normally is 5 to 10 or greater. The ratio can be reduced to 1 to 2 so that the final sample solution contains a lower salt content. This low-flux decomposition is referred to as sintering which involves solid-state reaction. Sodium peroxide is particularly suitable for decomposition by sintering.

#### (d) Ammonium iodide ( $\text{NH}_4\text{I}$ )

The effectiveness of  $\text{NH}_4\text{I}$  as a decomposition agent is attributed to its dissociation to form free hydrogen iodide. By heating  $\text{NH}_4\text{I}$  and geological samples at certain specified temperatures, Hg volatilizes as  $\text{HgI}_2$ , Sb as  $\text{SbI}_3$ , Sn as  $\text{SnI}_4$  and Bi as  $\text{BiI}_3$ . The iodides are thus separated from sample matrices and upon condensation are ready for analysis.

#### (e) Potassium and sodium pyrosulfate ( $\text{K}_2\text{S}_2\text{O}_7$ , $\text{Na}_2\text{S}_2\text{O}_7$ )

The pyrosulfate is an acidic weakly oxidizing agent and upon heating releases sulfur trioxide ( $\text{SO}_3$ ) which is the active component of the fusion. The mode of action of pyrosulfate is similar to that of concentrated  $\text{H}_2\text{SO}_4$ , but in this case a higher temperature can be reached. Fusion with  $\text{Na}_2\text{S}_2\text{O}_7$  is useful for decomposing mica and other layer silicates common in soils, leaving quartz and feldspar in the residue. The efficiency of pyrosulfate attack on silicates is a reflection of their mineralogy and degree of weathering. Potassium pyrosulfate has also been recommended to decompose the fluoride residue after digestion with HF.

## APPLICATION

Most acid digestion schemes include HF in the acid mixture. Fusion with  $\text{LiBO}_2$  is employed to decompose sample for 10 major elements and  $\text{HClO}_4$ -HF digestion for 15 trace elements. Sample solutions for major element determination can be diluted to lower the total dissolved salt content. Acid digestion is carried out either in open beakers or in pressure decomposition vessels. Digestion in open beakers is complete upon single or repeated fuming to get rid of the excess acids. Decomposition

in sealed PTFE-lined vessels generally takes place at 100 - 140 °C for 1 - 2 hour on a steam bath or in a drying oven. Lower temperature is usually accompanied by longer time of reaction in the sealed vessels.

For Au determination in geological materials, 10 g or more of the sample is used due to the low crustal abundance and inhomogeneous distribution of the element. Two acid mixtures, HBr-Br<sub>2</sub> and aqua regia, are in common use for sample decomposition after roasting the sample to destroy sulfides and organic matter. Once in solution, Au is extracted from HCl or HBr into methylisobutylketone (MIBK) before determination by AAS or GF-AAS; or the dissolved Au is isolated by coprecipitating with Te or Hg after reduction.

Digestion with multiple acids including HF, aqua regia and HBr-Br<sub>2</sub>, and fusion with lithium borates have all been used for sample decomposition preparatory to the determination of selected platinum group elements.

Due to the relatively low boiling points of the fluorides and chlorides of Se, As and Sb, overheating should be avoided during acid digestion. It has been recommended that the procedure is to keep As at the higher valency state and not to allow the acid digest to evaporate to dryness. The digestion is stopped when 2-3 ml of the digest remains. Acid digestion without HF is not expected to release the total amounts of As, Sb and Se from samples.

When acid mixtures containing HF are used, insoluble fluorides of REEs may remain in the precipitate. The precipitate should then be fused with NaOH or KHF<sub>2</sub> or K<sub>2</sub>S<sub>2</sub>O<sub>7</sub> and dissolved in acid. The combined solution is finally analyzed for the total REEs. Coprecipitation and/or ion exchange are often used to separate the REEs from the geological matrix to bring their concentrations up to the working range of the instrument and to remove possible spectral interferences.

## Recommended Analytical Method for Silicate Rock Samples

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### I. SILICON DIOXIDE

#### I-1. Summary

The powdered sample is fused with a mixture of sodium carbonate and boric acid, then dissolved by hydrochloric acid. The solution is warmed on a water bath until sub-solidified gel appears, then polyethylene oxide is added for the coagulation of silicon dioxide which is filtered. The precipitate is transferred into a Pt-crucible, then ignited. After cooling the crucible is weighed. Then, hydrofluoric acid is added to evaporate silicon dioxide in the crucible. Again, the crucible is ignited and weighed after cooling. Main silicon dioxide can be calculated from the difference of the weight before and after the evaporation. Remaining silicon dioxide in the solution can be determined by ICP-AES.

#### I-2. Reagents

- (1) Sodium carbonate anhydrous
- (2) Boric acid
- (3) Hydrochloric acid (1+1) and (1+50)
- (4) Cellulose powder (100 ~ 200 mesh)
- (5) Polyethylene oxide (Polymeric coagulant, molecular weight 250 ~ 500 million) (0.1%)
- (6) Sulfuric acid (1+1)
- (7) Hydrofluoric acid (50%<)
- (8) Sodium pyrosulfate ( $\text{Na}_2\text{S}_2\text{O}_7$ )
- (9) Standard stock solution of  $\text{SiO}_2$  (1 mg/ml): For the preparation, refer Appendix 1-3-2.

#### I-3. Analytical Procedure

(1) Weigh 0.5g (W g) of sample correctly in a Pt-dish (100 ml), to which 1.5g of  $\text{Na}_2\text{CO}_3$  and 0.2g<sup>\*1</sup> of  $\text{H}_3\text{BO}_3$  are added and mixed well. Then, the dish is ignited with a meker burner at 1000°C for 4 minutes<sup>\*2</sup>, so that the mixture can be fused.

<sup>\*1</sup> For the samples containing high  $\text{Al}_2\text{O}_3$ , the amounts of  $\text{Na}_2\text{CO}_3$  and  $\text{H}_3\text{BO}_3$  will need to be increased up to 2.0g and 0.3g respectively

<sup>\*2</sup> If the dish is ignited for more than 4 minutes, it will be difficult to dissolve the fused matter by  $\text{HCl}(1+1)$

(2) Cover the dish with a watch glass and leave it for cooling. After cooling the dish, add 20 ml of HCl (1+1) and dissolve the fused matter, then heat for 20 minutes<sup>\*3</sup> on a water bath.

(3) Add 0.05g of Cellulose powder and 5 ml of Polyethylene oxide (0.1%). Then using a glass rod having a flat tip stir the sub-solidified (gel) matter until the matter gets transparency<sup>\*4</sup>.

(4) Remove the watch glass from the dish without washing<sup>\*5</sup>. Filter the precipitate of the dish using No.5B filter paper, and wash 15 times by HCl (1+50) and 15 times by hot water. All filtrate is collected by a measuring flask (250 ml). The precipitate adhered to the inside wall of the dish can be removed by the filter paper using a finger and washing down.

(5) Transfer the precipitate together with the filter paper into a Pt crucible (30 ml). Then heat the crucible at low temperature until the filter paper is burnt to ash. After that, ignite the crucible at 1000 ~ 1050°C for one hour, then leave it in a desiccator for cooling. After cooling, weigh the crucible and ignite it again for 20 minutes. Weigh the crucible again (w1 g)<sup>\*6</sup>.

(6) Moisten the impure SiO<sub>2</sub> by water, add 2 ~ 3 drops of H<sub>2</sub>SO<sub>4</sub> (1+1) and 10 ml of HF, and then heat it on a sand bath up to dryness. After dry up, ignite the crucible at 1000 ~ 1050°C for 15 minutes and leave it in a desiccator for cooling. After cooling weigh the crucible (w2 g).

(7) Add 0.3g of Na<sub>2</sub>S<sub>2</sub>O<sub>7</sub> to the crucible and heat it gradually to fuse the residue in the crucible. After cooling, dissolve the fused matter by warm water and join it to the filtrate of procedure (4), which should be kept as solution A for the determination of soluble SiO<sub>2</sub> and some other elements.

Note: System diagram below is referred as a flow chart.

#### I-4. Calculation

$$\text{SiO}_2 (\%) = [(w1 - w2)/W] * 100$$

## II. ALUMINUM OXIDE

### II-1 Summary

A part of the solution A of I-3-(7) is allocated for the determination of Al<sub>2</sub>O<sub>3</sub>. M/50 CyDTA solution is added to react with aluminum and other elements. After the adjustment of pH to 5, the excess CyDTA is titrated by M/50 Zn standard solution using Xylenol Orange indicator. The amounts of CyDTA reacted are equivalent to R<sub>2</sub>O<sub>3</sub> content, from which Al<sub>2</sub>O<sub>3</sub> content is calculated after the determination of total Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>.

### II-2. Reagents

<sup>\*3</sup> If the solution remains unchanged after 10 minutes heating, take off the cover glass for easy evaporation till the solution is changed to gel.

<sup>\*4</sup> The number of times for stirring should be more than 200, otherwise washing the precipitate for the separation of other elements cannot be achieved.

<sup>\*5</sup> Water should not be added until first filtration complete. After that the cover glass will be washed.

<sup>\*6</sup> The weighing should be repeated until the difference of the weight is less than 0.5 mg from previous weight.

- (1) Nitric acid
- (2) Hydrochloric acid
- (3) M/50 CyDTA: A 7.28g of 1,2-Cyclohexanediamine-N,N,N',N'-tetraacetic acid is dissolved by 400 ml of 0.1N NaOH solution. Then the solution is made up to 1000 ml by water.
- (4) M/50 Zn Standard solution (refer Appendix 1-3-1-(3) for preparation)
- (5) Ammonium acetate solution,  $\text{CH}_3\text{CO}_2\text{NH}_4$ , (20%)
- (6) Hexamine (Hexamethylenetetramine)
- (7) MO solution (Methyl Orange) (0.1%)
- (8) XO solution (Xylenol Orange) (0.1%)

### II-3. Analytical Procedure

(1) Transfer 25 ml (W g) of the solution A of I-3-(7) into a conical flask (200 ml) and add 25 ml<sup>\*1</sup> of M/50 CyDTA solution precisely into it using a pipette.

(2) Add 1 drop<sup>\*\*2</sup> of MO indicator, then add  $\text{CH}_3\text{CO}_2\text{NH}_4$  (20%) until the solution is changed to orange. Leave it for 2 minutes.

(3) Add and dissolve 5g of Hexamine<sup>\*\*1</sup>, then make the solution 100 ml by water. Add 4 ~ 5 drops of XO indicator and titrate by M/50 Zn standard solution.

(4) Around the end point the titration should be carried out slowly and mixing the solution well. At the end point, yellow color of the solution will be changed to slightly reddish color (v1 ml).

(5) After determining Total  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$ <sup>\*\*4</sup> by the procedures of IV,  $\text{Al}_2\text{O}_3$  content can be calculated.

Note: System diagram below is referred as a flow chart.

### II-4. Blank test

Using reagents only, the procedure from II-3-(1) to II-3-(4) is carried out (v2).

### II-5. Calculation

$$\text{Al}_2\text{O}_3 (\%) = [(v1 - v2) \cdot 0.0010196/W] \cdot 100 - [(\text{Fe}_2\text{O}_3 + \text{TiO}_2) \cdot 0.638]$$

## III. FERROUS OXIDE

### III-1. Summary

To the sample in a Pt-crucible sulfuric acid and hydrofluoric acid are added. Then, keeping the insulation from air, the crucible is heated for dissolving the sample. After that the sample solution together with the crucible is transferred into the beaker having boric acid solution which is titrated immediately by  $\text{K}_2\text{Cr}_2\text{O}_7$  standard solution.

<sup>\*1</sup> If the sum of the amounts of  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$  is expected to be in a range of 30 ~ 40 %, the amount of M/50 CyDTA should be 30 ml.

<sup>\*\*2</sup> If more than 1 drop of MO is added, the end point of XO becomes unclear.

<sup>\*\*1</sup> By this procedure, pH of the solution will be adjusted to 5.

<sup>\*\*4</sup> M/50 CyDTA equivalent of these compounds will be subtracted from  $\text{R}_2\text{O}_3$

### III-2. Reagents

- (1) Sulfuric acid (1+1)
- (2) Hydrofluoric acid (50%)
- (3) Boric acid (saturated solution)
- (4) 4-Diphenylaminesulfonic acid sodium solution,  $C_{12}H_{10}NNaO_2S$ , (0.25%)
- (5) N/20 Potassium dichromate standard solution

### III-3. Analytical Procedure

(1) Weigh 0.5g (W g) of sample precisely into a Pt-crucible<sup>\*1</sup>. After moistening<sup>\*2</sup> the sample with small amount of water, add 5 ml of  $H_2SO_4$  (1+1) and 10 ml of HF. Cover the crucible properly.

(2) Heat the crucible for 10 ~ 15 minutes<sup>\*3</sup> on the sand bath which is already being heated to about 250°C in advance.

(3) Prepare the beaker (300 ml) with 200 ml of water, 20 ml of boric acid<sup>\*4</sup> (saturated solution) and 4 drops of Diphenylaminesulfonic acid-Na (0.25%). Keeping the closed cover<sup>\*5</sup>, transfer the crucible into the beaker.

(4) With continuous stirring the solution, titrate by N/20  $K_2Cr_2O_7$  standard solution. The solution will be colored claret (deep purplish red) with 1 drop of the standard solution at the end point (v ml).

Note. System diagram below is referred as a flow chart.

### III-4. Calculation

$$FeO (\%) = (0.003593 \cdot v/W) \cdot 100$$

## IV. OXIDES of Fe, Ti, Mn, Mg, Ca, Na, K and P

### IV-1. Summary

The powdered sample is decomposed by perchloric acid, nitric acid and hydrofluoric acid. After the solution is dried up, the residue is dissolved by hydrochloric acid and added lanthanum chloride. After making the solution to a constant volume, Fe, Ti, Mn, Mg, Ca, Na, K and P are determined with ICP-AES under the most suitable conditions for each element.

### IV-2. Reagents

- (1) Perchloric acid
- (2) Nitric acid
- (3) Hydrofluoric acid (50%)
- (4) Hydrochloric acid (1+1)

\*1 In advance, make the crucible able to cover without any gap.

\*2 The sample powder should not be solidified.

\*3 In the test experiments determine the most suitable heating time which leads to maximum consumption of  $K_2Cr_2O_7$  standard solution at the end.

\*4 This solution is added for masking the hydrofluoric acid

\*5 With the tongs of the reverse grip, lift up the crucible in soft touch and move into the beaker.

(5) Lanthanum chloride solution; 50g of  $\text{La}_2\text{O}_3$  is dissolved by 100 ml of  $\text{HCl}$  and made it to 1000 ml by water.

(6) Mixed standard stock solution; 1g equivalent each of  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ , 0.1g equivalent each of  $\text{MnO}$  and  $\text{P}_2\text{O}_5$  and 2g equivalent of  $\text{Al}_2\text{O}_3$  are aliquoted precisely from each standard stock solution into a measuring flask of 1000 ml. After mixing well, 10 ml of  $\text{HCl}$  (1+1) is added and made the solutions exactly to 1000 ml by water.

(7) Standard solution series for making the working curves of each elements; Exact 0.5 ml, 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 6 ml, 8 ml and 10 ml of the mixed standard stock solution of IV-2-(6) are aliquoted into the respective 100 ml measuring flask. Additionally half of the volume of the mixed solution is assigned to  $\text{TiO}_2$  (1 mg/ml) to be added to each flask. Then, 10 ml of Lanthanum solution prepared in IV-2-(5) and 5 ml of  $\text{HCl}$  (1+1) are also added to each flask. After that the solution of each flask should be made the constant volume (100 ml) precisely by water.

### IV-3. Analytical Procedure

(1) Weigh 0.1g (W g) of sample precisely in a Pt-dish (100 ml), to which 5 ml of  $\text{HClO}_4$ , 2 ml of  $\text{HNO}_3$  and 5 ml of  $\text{HF}$  are added. By heating on a sand bath, the sample will be decomposed.

(2) Heat the dish continuously. White fumes are generated<sup>\*1</sup> and  $\text{SiF}_4$  is expelled. Dry up the dish completely.

(3) After cooling, wash the inside wall of the Pt-dish with small amount of water and add 3 ml of  $\text{HClO}_4$ . Heat the dish again until slightly dry. Then, add 5 ml of  $\text{HCl}$  (1+1) and 10 ml of water. Cover it by a watch glass and heat for dissolving the residue.

(4) Leave the solution for cooling, then transfer it into a measuring flask (100 ml). Add 10 ml of  $\text{LaCl}_3$  solution<sup>\*2</sup> and make it to a constant volume by water.

(5) Select optimum conditions of ICP-AES such as the wavelength, power input to the plasma, argon gas flow rate and the height in the tail flame.

(6) Using the standard solution series of IV-2-(7), make a correlation curve between concentration and intensity of emission for each element to be analyzed. From the correlation curve and the measuring intensity of elements in the sample solution, calculate the concentration (C mg) of each element.

Note: System diagram below is referred as a flow chart.

### IV-4. Calculation

$$\text{Element (\%)}^{*3} = (C/1000/W) \times 100$$

## V. MOISTURE

### V-1. Summary

<sup>\*1</sup> If some solid materials were still remain at this stage, they may be due to coarse grain size of sample powder or low concentration of  $\text{HF}$  reagent. It should, therefore, be checked to find out reasons causing errors

<sup>\*2</sup> The same concentration of  $\text{La}$  should be added as an interference suppression agent to both standard and sample solutions.

<sup>\*3</sup> The mg unit of the standard solution is converted to g unit.



A 2 g of sample powder is weighed precisely into the weighing bottle (15 ml) of which the weight is already known. The bottle is then dried at 105 ~ 110°C for 2 hours in an air oven. After cooling the bottle, the decrease in weight is designated to be moisture (H<sub>2</sub>O-).

#### V-2. Apparatus

- (1) Weighing bottle
- (2) Air oven

#### V-3. Analytical procedure

(1) Put the weighing bottle (15 ml) for 30 minutes in an air oven maintaining the temperature of 105 ~ 110°C. Shift the cover of the bottle to the side during heating. After that, leave the bottle in a desiccator to cool without moisture. After cooling, weigh the bottle (w<sub>1</sub> g). Weigh 2g (W g) of sample and put into the bottle.

(2) Put the weighing bottle in the air oven maintaining the temperature of 105 ~ 110°C and shift the cover to side. After 2 hours, shift the cover to the original position and transfer the bottle into a desiccator. After cooling, weigh the bottle and again heat in the oven for 1 hour. After cooling, weigh the bottle again.

(3) Repeat the heating and weighing procedures until the constant weight (w<sub>2</sub> g)<sup>1</sup> is recorded.

Note: System diagram below is referred as a flow chart.

#### V-4. Calculation

$$\text{H}_2\text{O- (\%)} = \{[(w_1 + W) - w_2]/W\} * 100$$

## VI. COMBINED WATER

#### VI-1. Summary

A 0.5g of sample is put in the globular bottom of the glass made penfield tube. The sample in the tube is heated with burner for evaporating water which will be trapped at the cooling expanded part of the tube. The condensed water is weighed and the combined water (H<sub>2</sub>O+) is calculated by subtracting the moisture (H<sub>2</sub>O-).

#### VI-2. Apparatus

- (1) Penfield tube (softening temperature of 900°C, Fig.1)
- (2) Funnel (long-stem, Fig.1)
- (3) Meker gas burner
- (4) Parafilm

#### VI-3. Analytical procedure

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<sup>1</sup> The procedures should be repeated until the weigh difference is less than 0.5 mg.

(1) Weigh 0.5g of sample on a watch glass and, using a long-stem funnel, transfer it into the globular bottom of the glass made penfield tube. Then, the entrance of the tube is shut by parafilm and make a hole<sup>\*1</sup> in the center of film by a pin.

(2) Wrap the cloth wet with cold water around the expanded part of the tube. Then, hold the tube horizontally or slightly bottom up<sup>\*2</sup> on a steel stand. Keep the wrapped cloth cool by pouring cold water using a rough pipette.

(3) Heat the globular bottom of the tube for 3 minutes at low temperature by a meker gas burner. Then, heat it strongly for 5 ~ 6 minutes. Wrench off the softened globular bottom together with all sample powder using a crucible tongs<sup>\*3</sup>.

(4) Shut the bottom completely by fusing it taking care to avoid any crack. Cool it by holding the tube horizontally.

(5) Take away the wet cloth and wipe the moisture outside of the tube with dry cloth. After leaving for 15 minutes, weigh the tube (w1 g).

(6) Remove the parafilm<sup>\*4</sup> at the entrance of the tube and heat the tube at more than 100°C until the water inside the tube disappears. After cooling, weigh the tube together with the parafilm being removed (w2 g).

(7) After determining the moisture (H<sub>2</sub>O-) of the sample, calculate the combined water using the formula below.

Note: System diagrams below are referred as flow chart

#### VI-4. Calculation

$$\text{H}_2\text{O}^+ (\%) = [(w1-w2)/W]*100 - [\text{H}_2\text{O}^-(\%)]$$

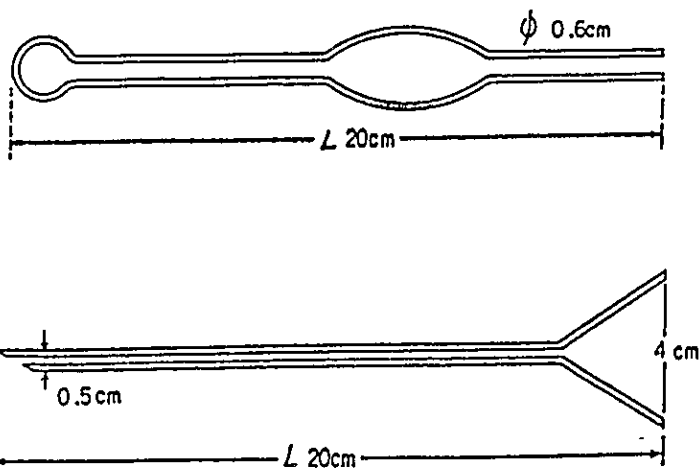


Figure 1. Penfield tube and long-stem funnel

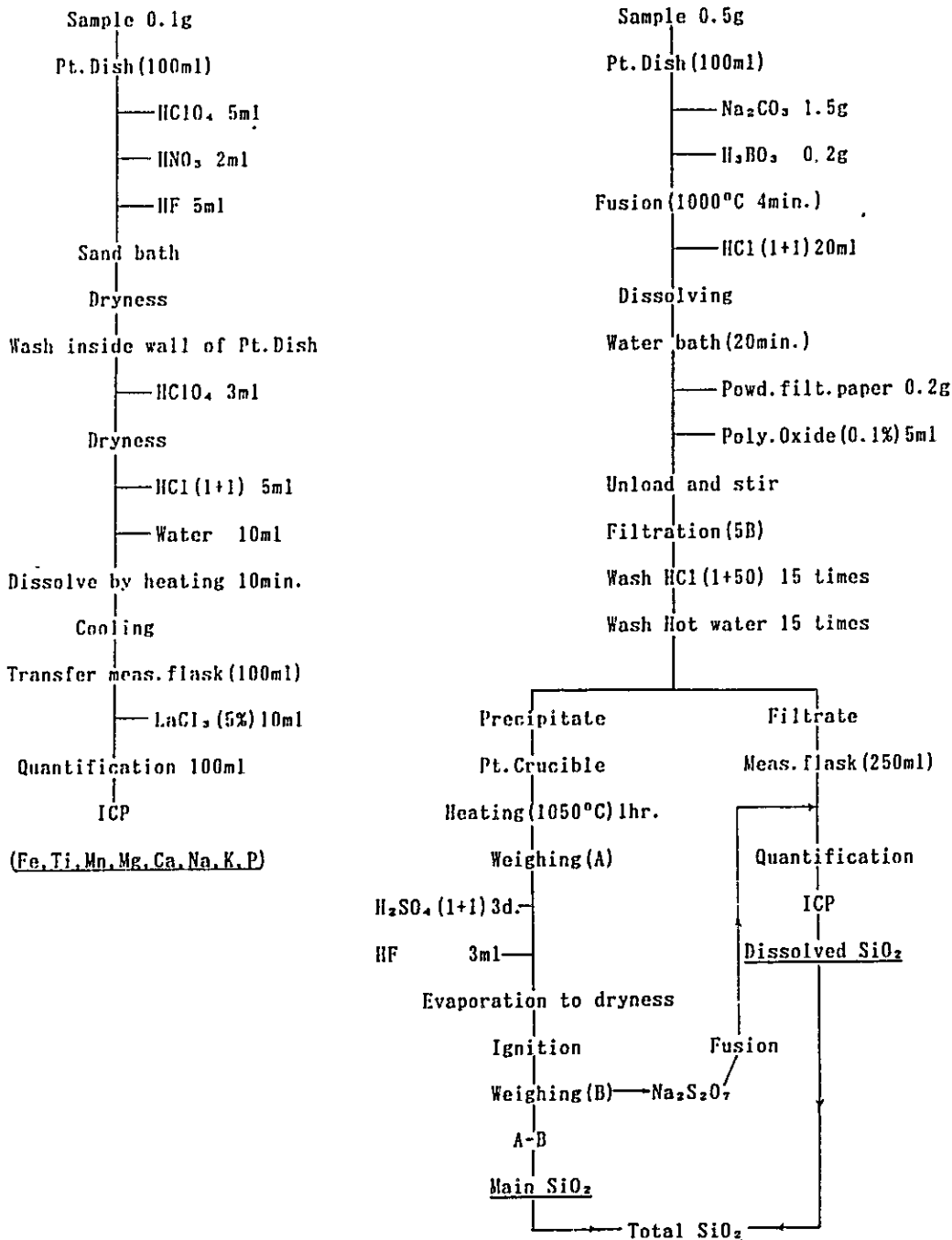
<sup>\*1</sup> If there was no hole, the inside sample will spout out when the tube is heated

<sup>\*2</sup> If the condensed water flows into the heated bottom, the glass tube will be broken.

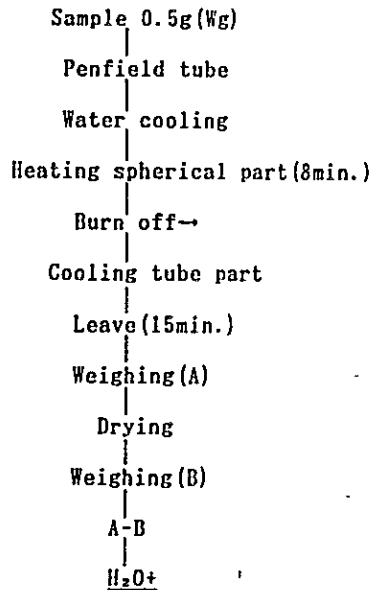
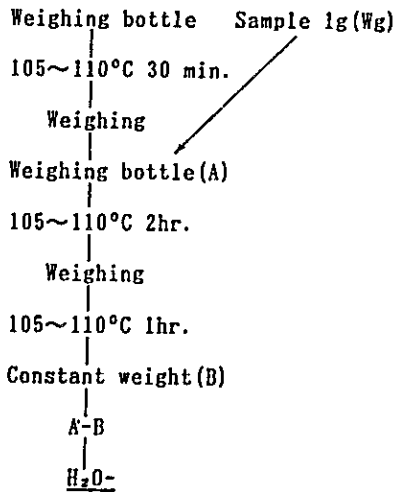
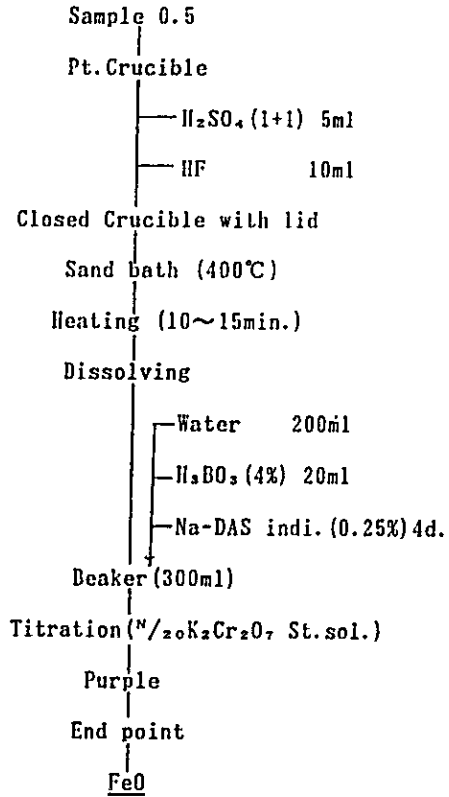
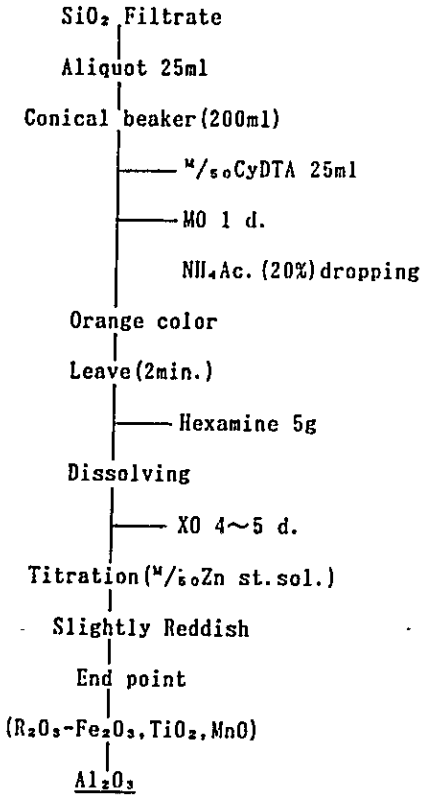
<sup>\*3</sup> The tips of crucible tongs should be heated in advance, otherwise cold tips will break the glass tube.

<sup>\*4</sup> This is to avoid the adherence of parafilm and make it easy for water to escape when the tube is heated

System Diagram of Rock Analysis ( $\text{SiO}_2, \text{Fe}, \text{Ti}, \text{Mg}, \text{Mn}, \text{Ca}, \text{Na}, \text{K}, \text{P}$ )



System Diagram of Rock analysis ( $\text{Al}_2\text{O}_3, \text{FeO}, \text{H}_2\text{O} \pm$ )



## Recommended Analytical Method of Chromite Ore

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### I. CHROMIUM OXIDE

#### I-1. Summary

Chromium ore sample is fused with sodium peroxide and then dissolved by hot water. All Cr ion in the sample solution will be of valency six after addition of sulfuric acid. By N/10 Ferrous standard solution, all Cr ions are reduced to their valence of three. Then excess ferrous ion in the solution can be determined by the titration with potassium dichromate standard solution.

#### I-2. Reagents

- (1) Sodium peroxide
- (2) Potassium permanganate solution (0.3 %)
- (3) Sulfuric acid (1+1)
- (4) Phosphoric acid
- (5) Silver nitrate solution (0.5 %)
- (6) Ammonium persulfate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$  solution (20 %)
- (7) Sodium chloride solution (5 %)
- (8) N/10 Iron(II) ammonium sulfate standard solution:  $[\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$  39.21 g/l
- (9) N/10 Potassium dichromate standard solution:  $[\text{K}_2\text{Cr}_2\text{O}_7]$  4.904 g/l
- (10) Sodium 4-Diphenylaminesulfonate (Na-DAS) (0.2 %) indicator

#### I-3. Analytical procedure

(1) Weigh 0.2 g (W g) of sample precisely into a zirconium crucible (50 ml). Add 5 g of  $\text{Na}_2\text{O}_2$  and mix it well<sup>\*1</sup>. With continuous shaking on a slow pace, heat the crucible at low temperature<sup>\*2</sup> until the solid material in the crucible becomes liquid.

(2) Ignite the crucible at  $600 \sim 700^\circ\text{C}$ <sup>\*3</sup> for about 5 minutes; any solid material should not be seen in the crucible when it is shaken. Leave the crucible for cooling.

<sup>\*1</sup> Mix only by moving the crucible around. Any tool like a glass rod should not be used, otherwise the sample will adhere to the rod.

<sup>\*2</sup> Initial strong heat will damage the crucible.

(3) Put the crucible in a tall beaker (500 ml). Add 150 ml of hot water<sup>\*3</sup> to the beaker and immediately after the addition cover the beaker with a watch glass. After the end of violent reaction heat the beaker using a water bath for about 15 minutes and then leave it for cooling.

(4) After cooling, wash the watch glass with water and remove it. With continuous stirring of the beaker, add  $H_2SO_4$  (1+1) dropwise till it becomes neutral<sup>\*4</sup>. Add another 20 ml of  $H_2SO_4$  (1+1) and remove the crucible from the beaker after washing it.

(5) Cover the beaker with a watch glass and heat for about 10 minutes for complete decomposition of  $H_2O_2$ .

(6) Add 5 ml of  $H_3PO_4$ , 0.5 ml of  $KMnO_4$  (0.3 %) and 10 ml of  $AgNO_3$  (0.5 %) successively to the beaker. Then make up solution to 200 ml by hot water, after that add 15 ml of  $(NH_4)_2S_2O_8$  (20 %) <sup>\*5</sup>. Boil the solution for about 5 minutes.

(7) Add 10 ml of  $NaCl$  (5 %) solution and heat the beaker, so that excess  $KMnO_4$  will be decomposed. Heat further for expelling  $Cl_2$  gas<sup>\*7</sup>. Cool the solution till room temperature and make up to 250 ml by water.

(8) By the addition of N/10  $FeSO_4(NH_4)_2SO_4$  standard solution<sup>\*8</sup> using a burette, Cr ion in the solution will be reduced from valence (VI) to (III) and accordingly the color of the solution will change from yellow to blue. After changing the color, add excess 5 ~ 10 ml (v1 ml) of the standard solution.

(9) Add 4 drops of Na-DAS (0.2 %) as an indicator and determine the excess  $FeSO_4$  by the titration with N/10  $K_2C_2O_7$  standard solution. At the end point (v2) of the titration, the solution will change its color from green to violet.

Note: System diagram below is referred as a flow chart.

#### I-4 Calculation

$$CrO (\%) = \{[(v1-v2)*0.002533] / W\} * 100$$

## II. IRON

### II-1. Summary

Sample is fused by sodium peroxide and dissolved by hot water. Iron in the sample will remain as residue, so that it can be separated from Cr, Al and other elements. The residue is dissolved by  $HCl$ . After concentrating the solution, iron will be reduced to the

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<sup>\*3</sup> This temperature is indicated by a wine red color of the crucible.

<sup>\*4</sup> If cold water is used, chromium ion of (VI) valency would be reduced to (III).

<sup>\*5</sup> When the solution approaches to neutral, no bubble can be seen.

<sup>\*6</sup> It is very important that the pink color of the solution is kept throughout this procedure. If the color is disappeared, then add some more  $(NH_4)_2S_2O_8$  solution.

<sup>\*7</sup> Chlorine gas can be detected by a smell. The gas will affect the titration if remains in solution.

<sup>\*8</sup> For the preparation of the standard solution and calculation of factor, appendix in this special issue can be referred.

(II) state by tin (II) chloride. After adding mercury (II) chloride, iron can be determined by the titration with potassium dichromate standard solution.

## II-2 Reagents

- (1) Sodium peroxide
- (2) Sodium hydroxide solution (2 %)
- (3) Hydrochloric acid (1+50)
- (4) Tin (II) chloride solution: During heating 100 ml of HCl, add 50 g of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and dissolve it. After cooling the solution, make it 500 ml with water.
- (5) Mercury (II) chloride (saturated)
- (6) Sulfuric acid (1+1)
- (7) Phosphoric acid (1+1)
- (8) N/10 Potassium dichromate standard solution: (refer Appendix for preparation)
- (9) Na-DAS indicator (0.2 %): [refer I-2-(10)]

## II-3. Analytical procedure

(1) Weigh 0.5 g (W g) of sample precisely into a zirconium crucible (50 ml). Fuse the sample with 5 g of  $\text{Na}_2\text{O}_2$ , by the same process as I-3-(1) and (2).

(2) Transfer the fused sample together with the crucible into a beaker (300 ml) and cover with a watch glass. Add 100 ml of hot water. After violent reaction is over, wash the crucible with water and take it out from the beaker. The crucible without any contamination should be left for the procedure (4).

(3) Boil the solution for about 5 minutes<sup>9</sup> for decomposition of  $\text{H}_2\text{O}_2$ . After cooling, separate the residue by filtration with a No.5B filter paper and wash the residue 2 times with NaOH (2 %) solution. The filtrate is discarded.

(4) Wash down the residue from the filter paper to the previously used beaker with water. The residue adhered to the inside wall of the crucible is also washed down to the same beaker with a small amount of HCl. Add 10 ml of HCl to the beaker and heat it for dissolving the residue. Using the previously used filter paper, separate insoluble matter from the solution by filtration. Wash the insoluble matter with hot HCl (1+50) solution<sup>10</sup>.

(5) Transfer all filtrate to a beaker (500 ml). Heat the beaker at low temperature until the volume of the solution is around 20 ml. Wash the inside wall of the beaker with water.

(6) With continuous heating and stirring the solution, add drop by drop  $\text{SnCl}_2$  solution (10 %) to the beaker till yellow color of the solution disappears. After that, add 1 drop excess of the  $\text{SnCl}_2$  solution and wash the inside wall of the beaker with water. Leave the beaker for cooling.

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<sup>9</sup> Boiling should be continued until no bubble appears

<sup>10</sup> After removing the brown color of Fe(III) ion from the filter paper, additional washing 3 times should be repeated

(7) Add 8 ml of  $\text{HgCl}_2$  (saturated) solution to the beaker\*<sup>11</sup> and mix it well by shaking. Make up the solution to 200 ml with water and then add 5 ml of  $\text{H}_2\text{SO}_4$  (1+1), 5 ml of  $\text{H}_3\text{PO}_4$  (1+1) and 4 drops of Na-DAS indicator.

(8) Immediately after the addition, titrate the solution with N/10  $\text{K}_2\text{Cr}_2\text{O}_7$  standard solution. At the end point (v ml) the solution will change its color to violet.

Note. System diagram below is referred as a flow chart.

#### II-4. Calculation

$$\text{Fe (\%)} = [v \cdot 0.005585 / W] \cdot 100$$

$$\text{FeO (\%)} = [v \cdot 0.007185 / W] \cdot 100$$

### III SILICA

#### III-1. Summary

Sample is decomposed by sulfuric acid and perchloric acid. After generating white fumes, hydrochloric acid is added and then the solution is heated to evaporate almost all Cr in the form of  $\text{CrO}_2\text{Cl}_2$ . The residue of the solution is separated by filtration and treated with hydrofluoric acid. The difference in weight before and after the IIF treatment is used for calculation of  $\text{SiO}_2$  content.

#### III-2. Reagents

- (1) Sulfuric acid (1+1)
- (2) Perchloric acid
- (3) Hydrochloric acid (1+10)
- (4) Hydrofluoric acid
- (5) Sodium pyrosulfate

#### III-3. Analytical procedure

(1) Weigh 0.5 g (W g) of sample precisely into a beaker (300 ml). Moisten the sample with water and add 10 ml of  $\text{H}_2\text{SO}_4$  and 20 ml of  $\text{HClO}_4$ . Heat the beaker on a sand bath.

(2) When the white fumes of  $\text{HClO}_4$  begin to come out violently, cover the beaker by a watch glass. Continue heating the beaker till the solution is stained by red color due to oxidation of  $\text{Cr}^{+12}$ . Leave the beaker for cooling.

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\*<sup>11</sup> If the addition of this reagent is in slow pace,  $\text{HgCl}_2$  may be reduced and Hg will be separated resulting in failure of the experiment

\*<sup>12</sup> If the covered watch glass is shifted to make some gap at the top of the beaker, the oxidation of Cr will be accelerated



(3) Add 5 ml of HCl to the beaker and heat it. By this procedure Cr will be evaporated as chromium (VI) oxychloride ( $\text{CrO}_2\text{Cl}_2$ , white fumes)<sup>\*13</sup>. Add again 5 ml of HCl to the beaker and heat it. Repeat this procedure until the red color of the solution disappears<sup>\*14</sup>.

(4) Continue heating the beaker for further 10 minutes<sup>\*15</sup> during which violent white fuming takes place. Then, leave the beaker for cooling. After cooling, add 50 ml of water to the beaker and heat it for dissolving the soluble matter.

(5) Separate the insoluble matter by filtration using a No.5B filter paper. All insoluble matter must be removed to the filter paper. Wash the insoluble matter 5 times by HCl (1+1) and next 5 times by hot water<sup>\*16</sup>. Receive all filtrate in a beaker (300 ml) and keep it for further process.

(6) Transfer the insoluble matter together with the filter paper into a Pt-crucible (30 ml). At first, heat the crucible at low temperature till the paper becomes ash, then ignite it for 1 hour at 1000 ~ 1050°C. Leave the crucible in a desiccator for cooling. After cooling, weigh the crucible. Ignite the crucible again for 15 minutes, and after cooling again weigh it. Repeat this procedure until a constant weight ( $w_1$  g) is obtained.

(7) Add 3 drops of  $\text{H}_2\text{SO}_4$  (1+1) and 5 ml of HF to the crucible, and heat it on a sand bath till drying up.

(8) Ignite the crucible for 10 minutes at 1000 ~ 1050°C, after that leave it in a desiccator for cooling. After cooling, weigh the crucible ( $w_2$  g).

(9) Add 1 g of  $\text{Na}_2\text{S}_2\text{O}_7$  to the crucible and fuse it. Dissolve the fused matter by hot water and transfer the solution into the same beaker of III-3-(5) which will be used for determination of Al and Mg.

Note: System diagram below is referred as a flow chart.

#### III-4 Calculation

$$\text{SiO}_2 (\%) = [(w_1 - w_2) / W] * 100$$

### IV. ALUMINUM OXIDE

#### IV-1. Summary

The filtrate in the  $\text{SiO}_2$  determination is added by ammonium hydroxide. Al and Fe are precipitated and can be separated from other elements by filtration. The precipitated matter is dissolved by hydrochloric acid and then Al will be separated from Fe using sodium hydroxide. The solution including Al is added by a constant amount of CyDTA

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\*13 Because of strong poisonous nature, the gas should carefully be exhausted

\*14 If during the repetition white fuming becomes weak, add some more  $\text{HClO}_4$

\*15 If the solution is dried up,  $\text{SiO}_2$  will adhere to the wall of the beaker resulting low value in  $\text{SiO}_2$  content.

\*16 Because of inadequate washing down of  $\text{HClO}_4$ , explosion may take place when the filter paper is burnt to ashes

standard solution and the pH of the solution is adjusted to 5. The excess CyDTA is determined by the back-titration using M/50 Zn standard solution. From the volume of the Zn standard solution used  $Al_2O_3$  content can be calculated.

#### IV-2. Reagents

- (1) Hydrochloric acid (1+1) and (1+10)
- (2) Ammonium hydroxide (28 ~ 30 %)
- (3) Sodium hydroxide solution (10 %) and (1 %)
- (4) Ammonium chloride solution (2 %)
- (5) Hydrogen peroxide (30 %)
- (6) Ammonium acetate solution (20 %)
- (7) Hexamine (Hexamethylenetetramine)
- (8) MO (Methyl orange) indicator: A 0.1 g of MO is dissolved by 100 ml of  $H_2O$
- (9) XO (Xylenol orange) indicator: A 0.1 g of XO is dissolved by 100 ml of  $H_2O$
- (10) M/50 CyDTA standard solution: A 7.28 g of CyDTA is dissolved by 400 ml of N/10 NaOH (or 1.6 g NaOH) and the solution is made to exact 1000 ml.
- (11) M/50 Zn standard solution. A 1.3076 g of Zinc metal (standard reagent) is added to 10 ml of water and 5 ml of  $HNO_3$  and then the solution is made to 1000 ml precisely.

#### IV-3. Analytical procedure

(1) Concentrate the solutions by heating after determining  $SiO_2$  (III-3-(5)) on a sand bath to approximate 150 ml. Add 3 drops<sup>\*17</sup> of  $H_2O_2$  to the solution and boil again for 10 minutes for decomposition of excess  $H_2O_2$ .

(2) With continuous stirring, add  $NH_4OH$  till a smell of ammonia remains at the top of the beaker. Add further 2 ml of  $NH_4OH$  to the beaker and boil for 2 minutes without stirring, so that all of Al, Fe and others are precipitated. Separate the precipitates by filtration using a No.5A filter paper and wash it 4 ~ 5 times with warm  $NH_4Cl$  (2 %) solution

(3) Receive the filtrate in a beaker (500 ml) and keep it for further processing. Wash down the precipitate into the previously used beaker by water. Add 20 ml of  $HCl$  (1+1) to the beaker and heat for dissolving the precipitate. Then, make the solution to about 100 ml

(4) Add  $NH_4OH$  again to the solution and repeat the procedures of (2) mentioned above. The previously used filter paper and beaker for the separation will be used in this procedure. All filtrate should be kept for the determination of Mg and Ca

(5) Wash down the precipitates into the same beaker previously used, and add 10 ml of  $HCl$  (1+1) to the beaker. Heat the beaker for dissolving the precipitate. Pass the solution through the filter paper previously used and wash the filter paper 10 times by  $HCl$  (1+10)<sup>\*18</sup>

<sup>\*17</sup> Remaining Cr(III) in the solution can be completely oxidized to (VI) by this  $H_2O_2$

<sup>\*18</sup> If there is a possibility of insoluble Al residue, then the filter paper should be burnt to ash and fused with 1 g of  $Na_2S_2O_7$ . Then, dissolve the fused matter and add this solution to the filtrate

(6) Concentrate the filtrate in procedure (5) by heating until its volume becomes about 80 ml. After cooling, transfer the solution into a measuring flask (100 ml) and make it to a constant volume (100 ml) by water.

(7) Allocate precise 20 ml of the solution from the flask to a beaker (200 ml). The solution for a blank test should be treated by the same process. Add water for making the solution to about 80 ml.

(8) Add NaOH (10 %) solution until Fe is precipitated and add further 10 ml of the NaOH solution. Boil the solution for 5 minutes and separate the precipitates by filtration using a No. 5A filter paper. Wash the precipitates 7 times with NaOH (1 %) solution and receive all filtrate into a conical flask (300 ml)<sup>\*19</sup>.

(9) Add 1 drop of MO indicator and acidify the solution by 1 ml of HCl (1+1). Add exact 25 ml<sup>\*20</sup> of M/50 CyDTA standard solution, after that add NH<sub>4</sub>Ac (20 %) till color of the solution changes to orange.

(10) Leave the solution for 2 minutes, then, add 5 g of Hexamine<sup>\*21</sup> and 1 ~ 2 drops<sup>\*22</sup> of XO indicator. Determine the excess CyDTA by the back-titration of M/50 Zn standard solution.

(11) At the end point (v1 ml) the color of the solution will change from yellow to slightly reddish. Determine the amount (v2 ml) of the Zn standard solution for blank test followed by the same procedure. Using the sample amount (W g) of III-3-(1), calculate the Al concentration.

Note: System diagram below is referred as a flow chart.

#### IV-4 Calculation

$$\text{Al}_2\text{O}_3 (\%) = \{[(v1 - v2) \cdot 0.0010196 / W] \cdot 100 / 20\} \cdot 100$$

### V. MAGNESIUM OXIDE

#### V-1. Summary

From the filtrate after separation of Fe(OH)<sub>3</sub> for the determination of Al<sub>2</sub>O<sub>3</sub>, a constant volume is aliquoted. After adjusting pH to 10, total MgO and CaO is determined by titration with M/40 EDTA standard solution. The MgO content can be calculated by subtracting CaO from the total.

#### V-2. Reagents

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\*19 The precipitates can be discarded

\*20 In the case of chromite ore sample, this amount of the standard solution will be sufficient to be surplus. If the amount is insufficient, the color of the solution turns red when XO is added. In this case add some more M/50 CyDTA standard solution and the same amount of the standard should also be added to the blank solution.

\*21 The pH of the solution becomes 5

\*22 More light color of the indicator is suitable for easy finding of the end point

- (1) Hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) solution (10 %)
- (2) Triethanolamine (1+1)
- (3) Potassium cyanide (KCN) solution (10 %)
- (4) Ammonium chloride (pH 10, buffer) solution: Mix 70 g of  $\text{NH}_4\text{Cl}$  and 570 ml of  $\text{NH}_4\text{OH}$  (28 %) and make them to 1000 ml with water.
- (5) Eriochrome Black T (BT) indicator: 0.2 g of BT is dissolved in a mixture of 15 ml of Triethanolamine and 5 ml of ethanol (95 %).
- (6) M/40 EDTA standard solution: 9.31 g of EDTA·2Na is dissolved by 1000 ml of water.
- (7) M/50 Zn standard solution: refer IV-2-(11).

### V-3. Analytical procedure

(1) Transfer the filtrate of IV-3-(3) and (4) into a measuring flask (250 ml) and make it to a constant volume of 250 ml by water. Then, aliquote precise 25 ml of the solution into a beaker (300 ml).

(2) Add 5 ml of  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (10 %) solution and 5 ml of triethanolamine (1+1). After mixing well, make the solution 100 ml in volume by water and add 2 ml of KCN (10 %) solution and 10 ml of the buffer solution of pH 10<sup>\*23</sup>.

(3) Add 2 drops<sup>\*24</sup> of BT indicator. Determine total amount of Mg and Ca by the titration using M/40 EDTA standard solution. At the end point (V ml), red color of the solution will completely change to blue color

(4) The factor (f) of the M/40 EDTA can be determined using M/50 Zn standard solution as follows Aliquot 25 ml ( $v_1$  ml) of the Zn standard solution into a beaker (300 ml) and add 2 ml of triethanolamine (1+1) and 10 ml of the buffer solution (pH 10). After making the solution 100 ml, follow the procedure (3) above for getting the end point ( $v_2$  ml).

(5) Calculate<sup>\*25</sup> the MgO content by subtracting the CaO content from the total. The CaO content can be determined by other method<sup>\*26</sup>.

Note: System diagram below is referred as a flow chart.

### V-4. Calculation

$$\text{factor of M/40 EDTA (f)} = (v_1 * 40 / 50) / v_2$$

$$\text{MgO (\%)} = \{[(V * 0.001008 * f) / W] * 250 / 25\} * 100 - \text{CaO (\%)}$$

<sup>\*23</sup> Addition of 10 ml of the buffer solution make sure that pH of the sample solution becomes 10

<sup>\*24</sup> Lighter color of the indicator makes easy finding of the end point. However, the amount of indicator is flexible depending on person to person

<sup>\*25</sup> The amount of sample (W g) is referred to III-3-(1).

<sup>\*26</sup> Because the CaO content of chromite ore is generally less than 0.1 %, Ca can be determined by ICP or AAS more precisely than titration method Theoretically CaO content should be converted to equivalent ml of M/40 EDTA In the case of minor amount of CaO in comparison to MgO, however, direct subtraction of CaO content makes no difference from the theoretical calculation.

## VI. OTHER ELEMENTS

### VI-1 Summary

Sample is weighed into a Teflon beaker and dissolved by heating with sulfuric acid and perchloric acid. After complete oxidation to Cr(VI), most of the Cr is evaporated by the repeated addition of hydrochloric acid. Remaining silicate is decomposed by hydrofluoric acid. All soluble salts are dissolved by hydrochloric acid and the solution is made to a constant volume. From the solution, Ti, Mn, Ca, Na, K, P and others are determined by ICP or AAS method.

### VI-2. Reagents

- (1) Sulfuric acid (1+1)
- (2) Perchloric acid
- (3) Hydrochloric acid
- (4) Hydrofluoric acid
- (5) Lanthanum chloride solution: 50 g of  $\text{La}_2\text{O}_3$  is dissolved by 100 ml of HCl, then make it 1000 ml by water.
- (6) Mixed standard stock solution: refer IV-2-(6) in the recommended analytical method for rock samples.
- (7) Standard solution series for calibration curves: refer IV-2-(7) in the recommended analytical method for rock samples.

### VI-3. Analytical procedure

(1) Weigh 0.1 g (W g) of sample precisely into a Teflon beaker (300 ml) and moisten it with water. Add 5 ml of  $\text{H}_2\text{SO}_4$  (1+1) and 20 ml of  $\text{HClO}_4$  to the beaker and heat the beaker on a sand bath for dissolving the sample.

(2) When white fumes are seen in the beaker, cover the beaker with a Teflon watch glass. Continue the heating with violent white fumes until the solution is stained by brown ~ red color due to the oxidation of Cr. After that, leave the beaker for cooling.

(3) Add 5 ml of HCl to the beaker and heat<sup>\*27</sup> it again, by which the evaporation of chromium (VI) oxychloride ( $\text{Cr}_2\text{O}_2\text{Cl}_2$ )<sup>\*28</sup> will take place. Repeat the addition of HCl and heating for generating white fume<sup>\*29</sup> until the brown ~ red color of the solution disappears.

(4) After cooling, remove the Teflon watch glass and add 5 ml of HF. Heat it again on a sand bath for decomposition of silicate. Generate thick white fumes of sulfuric acid and then leave it for cooling.

<sup>\*27</sup> For accelerating the oxidation of Cr, it is better to shift slightly the cover glass of the beaker.

<sup>\*28</sup> Because of strong poison of the fumes, careful exhaustion of the gas is needed

<sup>\*29</sup> When the generation of white fume becomes less, then add some more  $\text{HClO}_4$  and continue heating.

(5) Add 5 ml of HCl and 20 ml of water to the beaker. Heat the beaker for dissolving soluble matter. After cooling the beaker, transfer the solution into a measuring flask (100 ml). Add 10 ml of LaCl<sub>3</sub> (5 %) solution to the flask and make the solution to a constant volume.

(6) Determine the optimum conditions of ICP-AES<sup>\*30</sup> measurements such as most suitable wavelength, power of plasma generation, carrier gas flow rate and measuring height above the work coil (radiofrequency induction coil).

(7) Using the standard solution series of VI-2-(7), make the calibration curves for each target element. Measure the emission intensities of elements in the sample solution (VI-3-(5)). From the calibration curves and the measurement data of emission spectrometer, the concentration (C mg) of elements can be determined.

Note: System diagram below is referred as a flow chart.

#### VI-4. Calculation

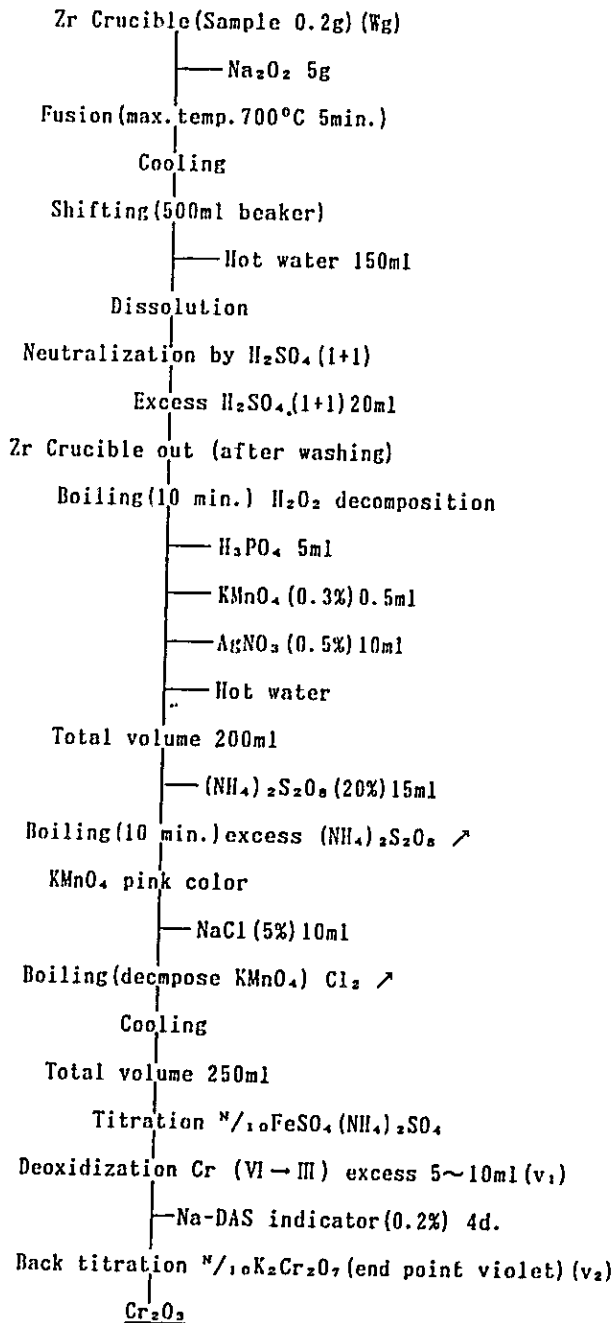
$$\text{Element (\%)}^{*31} = (C/1000/W) * 100$$

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<sup>\*30</sup> In the case of AAS measurements, specific hollow cathode lamps are used. However, Ti and P are difficult to be analyzed by this method.

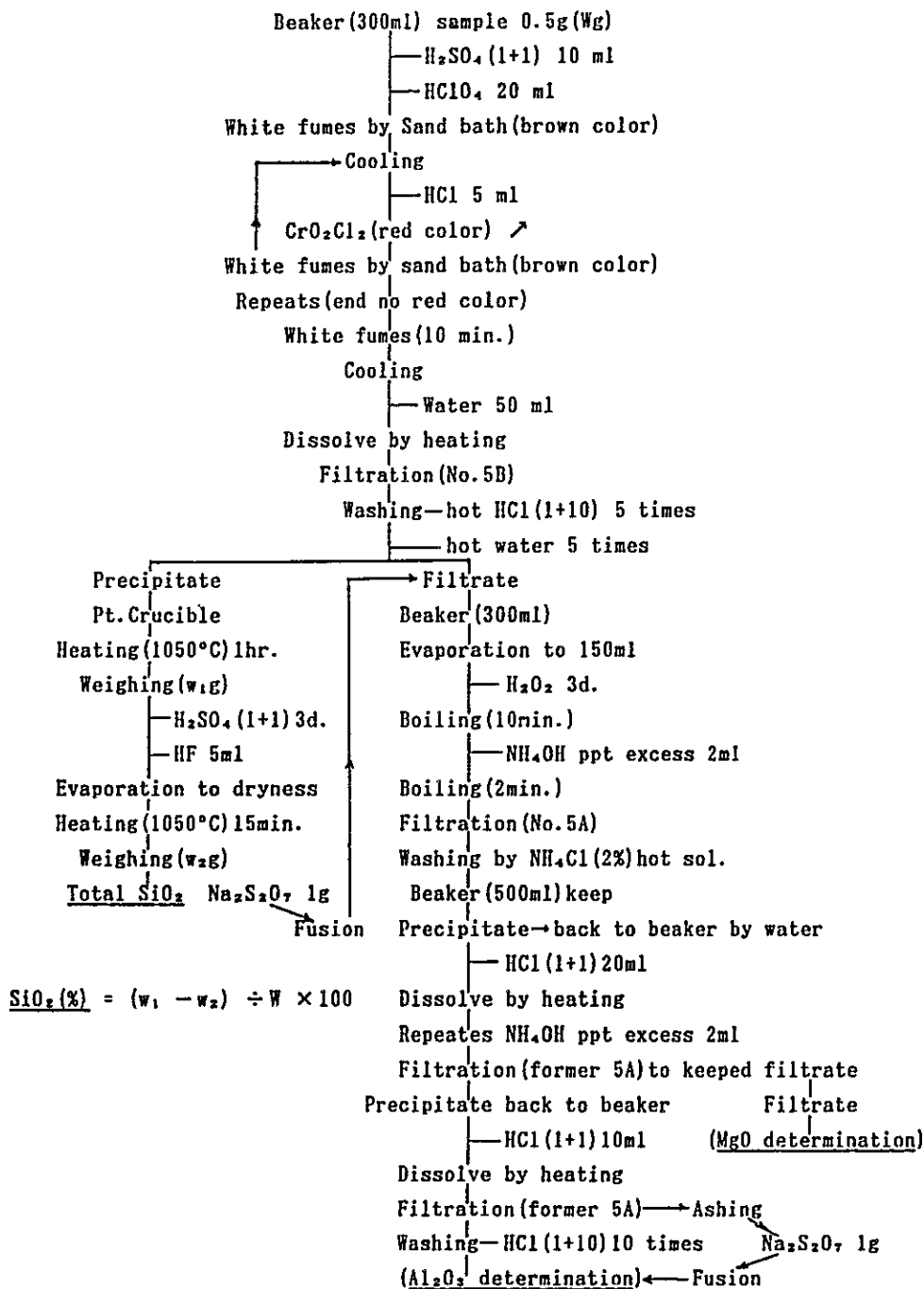
<sup>\*31</sup> The mg unit of standard solution is converted to g unit.

System Diagram of Chromite (PCr-1) Analysis ( $\text{Cr}_2\text{O}_3$ )



$$\text{Cr}_2\text{O}_3 (\%) = (v_1 - v_2) \times 0.002533 \div W \times 100$$

System Diagram of Chromite (PCr-1) Analysis(SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO) I

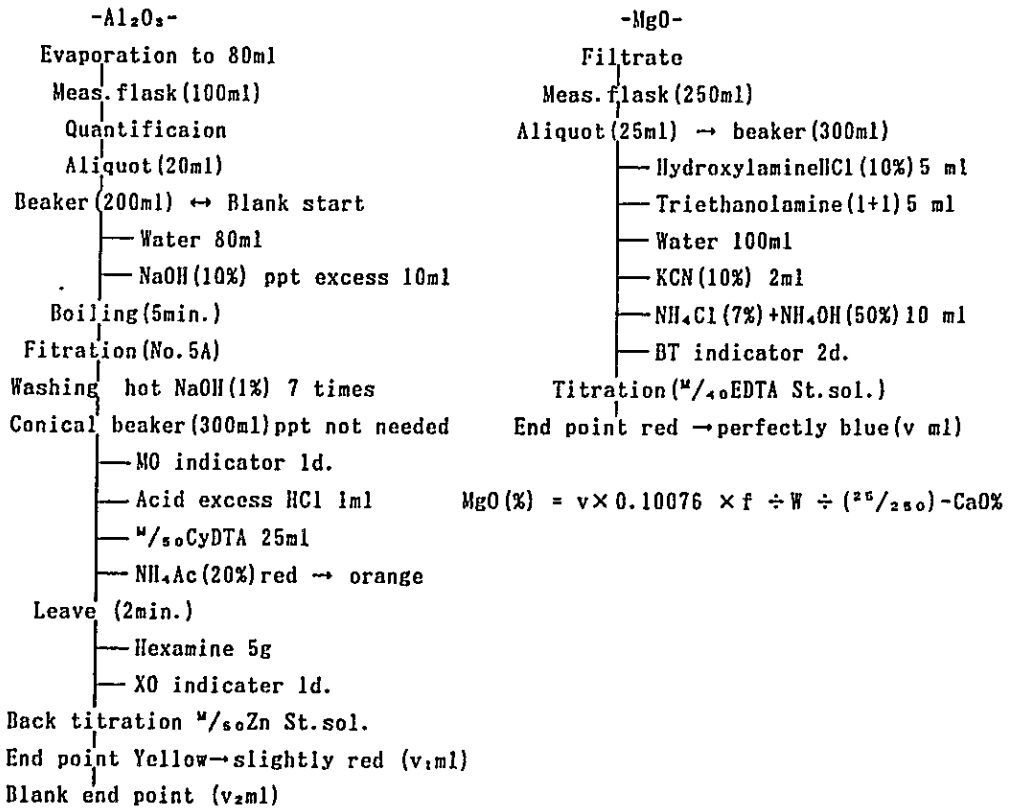


$$\text{SiO}_2(\%) = (w_1 - w_2) \div W \times 100$$

(next page)



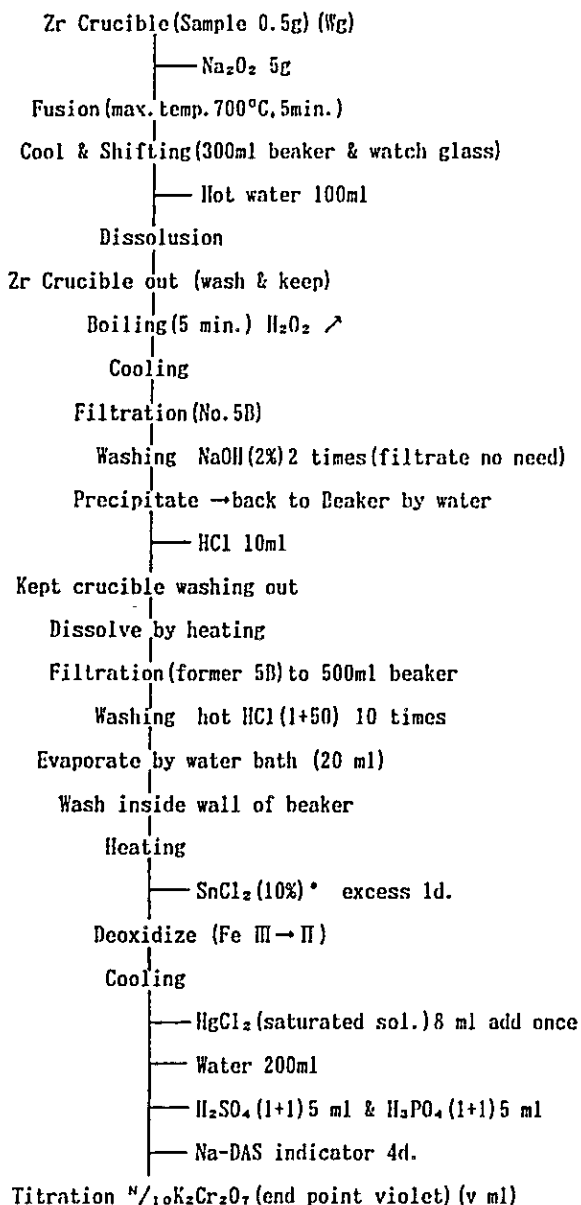
System Diagram of Chromite (PCr-1) Analysis ( $Al_2O_3, MgO$ ) II



$$MgO (\%) = v \times 0.10076 \times f \div W \div (\frac{25}{250}) - CaO\%$$

$$Al_2O_3 (\%) = (v_2 - v_1) \times 0.10196 \times f \div W \div \frac{20}{100}$$

System Diagram of Chromite (PCr-1) Analysis (Fe)

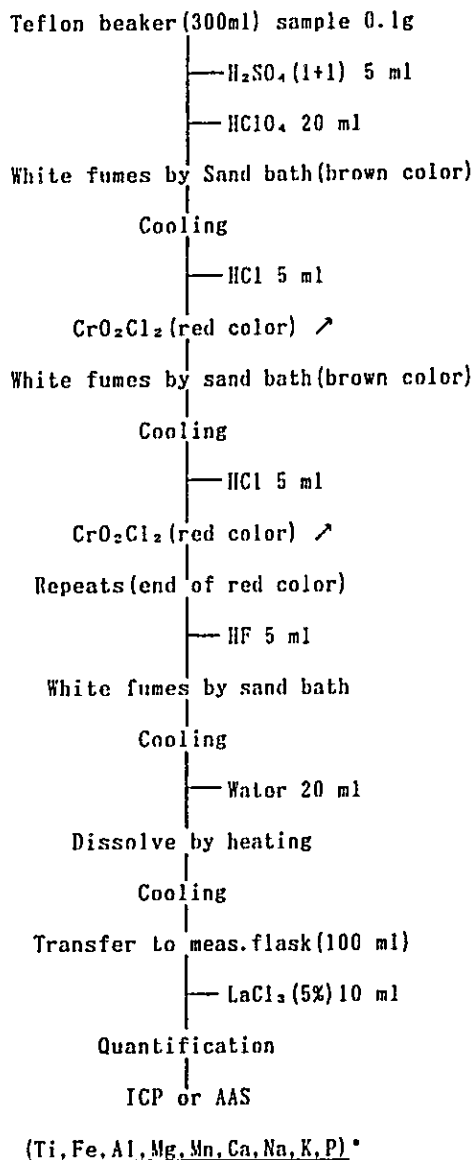


$$\text{Fe}(\%) = v \times 0.5585 \div W$$

$$\text{FeO}(\%) = v \times 0.7185 \div W$$

\*  $\text{HCl}$  100ml +  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  50g → 500ml by water

System Diagram of Chromite(PCr-1) Analysis (Ti, Al, Fe, Mg, Mn, Ca, Na, K, P)



\* 5 % over elements to be analyzed by wet analysis

## Recommended Analytical Method for Phosphorite Ore Samples

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### I. OXIDES of Ti, Fe, Al, Mg, Mn, Na, K, Ca and P

#### I-1. Summary

The powdered samples are weighed into a Pt dish and are decomposed by perchloric acid, nitric acid and hydrofluoric acid. After drying up the solution, the residue is dissolved by hydrochloric acid. Then, lanthanum chloride solution is added to the solution. The oxides of Ti, Fe, Al, Mg, Mn, Na and K are determined by ICP-AES. A small amount of the solution is aliquoted and diluted with water, from which CaO and P<sub>2</sub>O<sub>5</sub> are estimated roughly by ICP-AES<sup>\*1</sup>. The estimated value of these elements will be referred to the volumetric analysis of the same elements.

#### I-2. Reagents

- (1) Perchloric acid
- (2) Nitric acid
- (3) Hydrofluoric acid
- (4) Hydrochloric acid
- (5) Lanthanum chloride solution (5 %): A 50g of La<sub>2</sub>O<sub>3</sub> is dissolved by 100 ml of HCl. Then, the solution is diluted to 1000 ml with water.
- (6) Mixed standard stock solution (1 mg/ml): Each 1g equivalent of TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, MnO, Na<sub>2</sub>O and K<sub>2</sub>O are aliquoted precisely from respective standard stock solution to a measuring flask (1000 ml) and are mixed well. Then, 10 ml of HCl (1+1) is added to the flask and the volume of solution is made precisely to 1000 ml with water.
- (7) Standard solution series for calibration: From the stock solution above, exact 0.5 ml, 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 6 ml, 8 ml and 10 ml are aliquoted into the respective 100 ml measuring flask. A 10 ml of LaCl<sub>3</sub> solution (5 %)<sup>\*2</sup> and 5 ml of HCl (1+1) are added to each flask, then each flask is filled with water upto the mark precisely.
- (8) Standard solution series for CaO and P<sub>2</sub>O<sub>5</sub> calibration: Exact 1 ml, 2 ml, 3 ml, 4 ml, 5 ml and 6 ml of the standard stock solution (1 mg/ml, refer Appendix I-3-2 for preparation) of CaO and P<sub>2</sub>O<sub>5</sub> are aliquoted into the respective 100 ml flask. A 10 ml of LaCl<sub>3</sub> solution (5 %) and 5 ml of HCl (1+1) are added to each flask, then each flask is filled with water upto the mark precisely.

<sup>\*1</sup> Because of large dilution ratio, accurate value of these elements is obtained by volumetric method

<sup>\*2</sup> The reagent acts as a inhibitor to chemical interference in the atomization of target elements.

### I-3. Analytical procedure

(1) Weigh 0.2g (W g) of sample precisely into a Pt dish (100 ml). Add 5 ml of HClO<sub>4</sub>, 2 ml of HNO<sub>3</sub> and 5 ml of HF successively to the dish. Heat the dish on a sand bath for decomposing the sample.

(2) Continue heating the dish until the solution is dry. After cooling, wash the inside wall of the Pt dish with a small amount of water. Then, add 3 ml of HClO<sub>4</sub> to the dish and heat it again till dryness. Add 5 ml of HCl (1+1) and 10 ml of water. Cover the dish with a watch glass. Then, heat the dish again for dissolving residue.

(3) After cooling, transfer the solution of the dish into a measuring flask (100 ml). Add 10 ml of LaCl<sub>3</sub> (5 %) solution to the flask and make the solution to exact 100 ml with water. This solution is assigned as Solution A.

(4) Aliquot 5 ml of the Solution A precisely into another measuring flask (100 ml). Add 5 ml of HCl (1+1) and 10 ml of LaCl<sub>3</sub> solution (5 %) to the flask and make the solution to exact 100 ml with water. This solution is assigned to Solution B.

(5) Select the optimum conditions of ICP-AES measurements such as most suitable wavelength, power of plasma generation, carrier gas flow rate and measuring height above radio frequency induction coil for each element.

(6) Using the standard solution series of I-2-(7), make the calibration curves for each target element. Measure the emission intensities of elements in the sample Solution A. From the calibration curves and the measurement data of emission spectrometer, the concentration (C1 mg) of elements can be determined.

(7) Using the standard solution series for CaO and P<sub>2</sub>O<sub>5</sub> {I-2-(7)}, make the calibration curves for each element. Measure the emission intensities of elements in the sample Solution B. From the calibration curves and the measurement data of emission spectrograph, the concentration (C2 mg) of elements can be determined.

Note: System diagram below is referred as a flow chart.

### I-4. Calculation

$$\text{TiO}_2 \dots \text{K}_2\text{O} (\%)^{*3} = (C1/1000/W)*100$$

$$\text{CaO or P}_2\text{O}_5 (\%) = [C2/1000/(5/100)/W]*100$$

## II SILICON DIOXIDE

### II-1. Summary

The powdered samples are decomposed by HClO<sub>4</sub> saturated with H<sub>3</sub>BO<sub>3</sub>. After evolving white fumes of HClO<sub>4</sub>, the soluble residue is dissolved by HCl and the remains are separated by filtration. Then, the residue is ignited and weighed. SiO<sub>2</sub> in the residue is expelled selectively by HF. The residue is ignited again and weighed. Decrease in weight gives the value of SiO<sub>2</sub> content.

### II-2. Reagents

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\*3 The mg unit of the standard solution is converted to the g unit.

- (1) Boric acid
- (2) Mixture of perchloric acid and boric acid. 500 ml of  $\text{HClO}_4$  (1+2) is heated to  $50^\circ\text{C}$  and these 25 g of boric acid<sup>\*4</sup> is added.
- (3) Hydrochloric acid (1+1) and (1+50)
- (4) Hydrofluoric acid.

### II-3. Analytical procedure

(1) Weigh 0.5g (W g) of sample precisely into a beaker (200 ml). Add 30 ml of the acid mixture of II-2-(2) to the beaker and heat it on a sand bath for dissolving the sample.

(2) As soon as the white fumes of  $\text{HClO}_4$  start coming out of the beaker, cover it with a watch glass. Continue heating the beaker with violent white fumes for 5 minutes. After cooling, wash down the inside wall of the beaker with a small amount of water. Then, again heat the beaker until violent white fumes evolve for 5 minutes<sup>\*5</sup>.

(3) After cooling, add 5 ml of  $\text{HCl}$  (1+1) and 30 ml of water to the beaker. Heat the beaker for dissolving soluble matter. Separate the residue from solution by filtration using a No. 6 filter paper. Wash the residue 5 times with  $\text{HCl}$  (1+50) and 10 times<sup>\*6</sup> with hot water. Collect the filtrate and washing water in a measuring flask (250 ml) and then make the solution to a constant volume (250 ml) by water.

(4) Transfer the residue along with the filter paper to a Pt crucible (30 ml). Heat the crucible at low temperature until the paper converts to ash. Then, ignite the crucible at  $1050^\circ\text{C} \pm 20^\circ\text{C}$  for 1 hour. Leave the crucible in a desiccator for 20 ~ 30 minutes. Then, weigh the crucible (w1 g).

(5) After moistening the residue with a small amount of water, add 5 drops of  $\text{HClO}_4$  and 3 ml of  $\text{HF}$  to the crucible and heat the crucible till dryness on a sand bath. Ignite the crucible at  $1000^\circ\text{C}$  for 10 minutes. Then, leave it in a desiccator for cooling. Weigh the crucible to obtain the second weight (w2 g).

Note: System diagram below is referred as a flow chart.

### II-4. Calculation

$$\text{SiO}_2 (\%) = [(w1 - w2)/W] * 100$$

## III. CALCIUM OXIDE

### III-1. Summary

The sample solution aliquoted from the filtrate above {II-3-(3)} of  $\text{SiO}_2$  determination is added by M/40 EDTA standard solution of 3/4 equal to amount required as rough estimate of CaO contents {I-3-(7)}, so that precipitation of calcium phosphate can be prevented. After adjusting pH to 13, remaining CaO is titrated by

\*1 Boric acid reacts with fluorine in phosphate sample forming complex ion, so the interference of fluorine can be prevented

\*5 If the solution is dried up,  $\text{SiO}_2$  will be adhered to the wall of the beaker causing low result. Therefore, the solution should not be dried up

\*6 If  $\text{HClO}_4$  remains in the residue, explosion may take place during ashing of the filter paper

M/40 EDTA standard solution. CaO content can be calculated by the sum of the standard solution consumed.

### III-2 Reagents

- (1) Triethanolamine (1+1)
- (2) Potassium cyanide solution (10 %)
- (3) Potassium hydroxide solution (25 %)
- (4) NN indicator: A 1g of 2-Hydroxy-1-(2-Hydroxy-4-Sulfo-1-Naphthylazo)-3-Naphthoic acid is mixed with 50g of  $K_2SO_4$ .
- (5) XO indicator: 0.1g of Xylenol Orange is dissolved by 100 ml of water.
- (6) M/40 EDTA standard solution. A 9.31g of EDTA·2H<sub>2</sub>O is dissolved to 1000 ml of water.
- (7) M/40 Zn standard solution: A 1.6345g of Zn metal (standard reagent) is weighed precisely and is dissolved with 5 ml of HNO<sub>3</sub> and heating. After cooling, the solution is diluted precisely up to 1000 ml by water.
- (8) Hexamine

### III-3. Analytical procedure

(1) Aliquot precise 25 ml (V ml) of the filtrate (II-3-(3)) to a beaker (500 ml). Add 5 ml of triethanolamine (1+1) to the solution.

(2) Make up the solution in the beaker to approximate 300 ml by water. Then, add 2 ml of KCN solution (10 %) to the beaker and mix the solution well. Using a burette, add M/40 EDTA standard solution of three fourth of expected volume from the result<sup>\*7</sup> of I-3-(7) to the beaker and mix the solution well.

(3) Add 10 ml<sup>\*8</sup> of KOH solution (25 %) to the beaker for adjusting the pH to 13<sup>\*\*</sup>. Add approximate 0.1g of NN indicator and titrate the solution with M/40 EDTA standard solution at a slow pace<sup>\*10</sup>. At the end point (v1 ml) of the titration, the color of the solution will be changed from red to perfect blue and show no more change of the color by further shaking.

(4) Aliquot precise 20 ml (v2 ml) of M/40 Zn standard solution to a conical flask (200 ml) and add 5g of Hexamine<sup>\*11</sup> to the solution. After dissolving the reagent, add 1 drop of XO indicator and titrate at a slow pace with M/40 EDTA standard solution. At the end point (v3 ml), the color of the solution will be changed from claret to bright yellow.

Note. System diagram below is referred as a flow chart.

### III-4. Calculation

$$\text{Factor of M/40 EDTA (f)} = v2/v3$$

$$\text{CaO (\%)} = 0.001402 * f * v1 * \{(250/W)/V\} * 100$$

<sup>\*7</sup> This is a rough estimation, because of large dilution ratio

<sup>\*8</sup> By the addition of this amount of KOH, the pH of the solution becomes 13

<sup>\*9</sup> In this pH condition, Mg is precipitated as hydroxide and does not react with EDTA

<sup>\*10</sup> Even Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> is precipitated, the compound will be converted to EDTA complex during the slow pace titration

<sup>\*11</sup> By this amount of the reagent, pH of the solution becomes 5. It should be noticed that the pH does not become 5 if the reagent is impure

## IV. PHOSPHORUS PENTOXIDE (P<sub>2</sub>O<sub>5</sub>)

### IV-1. Summary

A constant amount is aliquoted from the solution after separation of SiO<sub>2</sub> {II-3-(3)} and is acidified by adding HNO<sub>3</sub>. Beside the solution, some blank solutions are added by standard P<sub>2</sub>O<sub>5</sub> solution for calibration. All these solutions are added by metavanadate solution and molybdate solution for obtaining the yellow color of phosphovanadomolybdic acid. Intensity of the color is measured spectrophotometrically.

### IV-2. Reagents

- (1) Nitric acid
- (2) Ammonium metavanadate solution: A 1.25g of NH<sub>4</sub>VO<sub>3</sub> is dissolved by 100 ml of hot water. After cooling the solution, 5 ml of HNO<sub>3</sub> is added and it is made up to 250 ml by water.
- (3) Ammonium molybdate solution: A 12.5g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O is dissolved by 250 ml of warm water.
- (4) P<sub>2</sub>O<sub>5</sub> standard solution (1.0 mgP<sub>2</sub>O<sub>5</sub>/ml): KH<sub>2</sub>PO<sub>4</sub> is dried at 110 °C for 3 hours. After cooling in a desiccator, an exact 0.4794g of the reagent is dissolved into a precise 250 ml of water.

### IV-3. Analytical procedure

(1) Aliquot 5 ml (V ml)<sup>\*12</sup> of sample solution from the solution (250/Wg) after separation of SiO<sub>2</sub> [II-3-(3)] into a beaker (100 ml).

(2) Add 5 ml of HNO<sub>3</sub> to the beaker. Heat the beaker till dryness. Add precise 4.0 ml<sup>\*13</sup> of HNO<sub>3</sub> and 20 ml of water to the beaker. Cover the beaker with a watch glass and heat it for dissolving residue. After cooling, transfer the solution to a measuring flask (100 ml)<sup>\*14</sup>.

(3) To other four measuring flasks (100 ml), aliquot 5 ml each of the blank solution by the same procedure of the SiO<sub>2</sub> determination. Add 0.0, 2.0, 4.0 and 6.0 ml of P<sub>2</sub>O<sub>5</sub> standard solution {IV-2-(4)} to the flasks, respectively. Then, add precise 5.0 ml of NH<sub>4</sub>VO<sub>3</sub> to both sample and standard series solutions. Dilute each solution to around 80 – 85 ml<sup>\*15</sup> by water.

(4) Add 10 ml of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> to each solution and add water to the mark of the flask. After mixing the solution well, leave the flasks for 30 minutes. Measure the absorbance of each solution at the 460 nm wavelength of spectrophotometer in comparison with those of water. Using the calibration curve obtained from standard series solutions, determine the concentration (C) of P<sub>2</sub>O<sub>5</sub> in the sample solution.

<sup>\*12</sup>The amount of the sample solution should be changed according to phosphorus content. It is recommended that the P<sub>2</sub>O<sub>5</sub> content of the aliquoted solution should be less than 5mg.

<sup>\*13</sup>The solution should have a constant HNO<sub>3</sub> concentration.

<sup>\*14</sup>In this stage the volume of the solution should be less than 60 ml.

<sup>\*15</sup>In order to minimize the effect of acid concentration to measurement, this volume is recommended at this stage



Note: System diagram below is referred as a flow chart.

#### IV-4. Calculation

$$P_2O_5 (\%)^{16} = [C/1000*(250/W)/V]*100$$

### V. TOTAL SULFUR

#### V-1. Summary

Powdered sample is decomposed by bromine water and HNO<sub>3</sub>. After expelling HNO<sub>3</sub> by HCl, insoluble matter is separated by filtration. To the filtrate barium chloride solution is added for the precipitation of BaSO<sub>4</sub>. The precipitate is separated by filtration and ignited to ash. From the weight of the ash, total S or SO<sub>3</sub> in the sample can be calculated.

#### V-2. Reagents

- (1) Bromine water
- (2) Nitric acid
- (3) Hydrochloric acid
- (4) Barium chloride solution (10 %)

#### V-3. Analytical Procedure

(1) Weigh 2g (W g) of powdered sample precisely into a beaker (200 ml). Add 20 ml of bromine water and 20 ml of HNO<sub>3</sub> to the beaker. Cover the beaker with a watch glass and heat it at a slow pace<sup>17</sup> on a sand bath with increasing temperature.

(2) Continue heating till dryness. After cooling, add 15 ml of HCl to the beaker and heat it till dryness. After cooling, again add 15 ml of HCl to the beaker and heat it till dryness. Repeat this procedure till HNO<sub>3</sub> is expelled completely<sup>18</sup> from the beaker.

(3) After cooling, add 5 ml of HCl (1+1) and 50 ml of warm water and heat it for dissolving soluble matter. The insoluble residue is separated by filtration using a No. 6 filter paper. Wash the residue 5 times by HCl (1+50) and then 5 ~ 6 times by hot water. Collect the washing liquid and filtrate in a beaker (300 ml) and dilute the solution to 250 ml by water.

(4) Boil the solution gently and add 10 ml of hot BaCl<sub>2</sub> solution at a slow pace and with continuous stirring by a glass rod with silicon rubber. Continue heating for 15 minutes, then leave the beaker at a warm place.

(5) If precipitate is comparatively large in amount, then leave<sup>19</sup> the beaker for 30 minutes at a warm place. Separate the precipitate by filtration using a No. 6 filter paper. Wash the precipitate 5 times by HCl (1+50) and then 8 times by warm water. Transfer the precipitate along with the filter paper to a porcelain crucible (15 ml).

<sup>16</sup>The mg unit is converted to the g unit.

<sup>17</sup>If the solution is heated strongly at first stage, free sulfur will appear due to inadequate oxidation.

<sup>18</sup>If HNO<sub>3</sub> remains in this procedure, the addition of BaCl<sub>2</sub> in following procedure may result in the formation of Ba(NO<sub>3</sub>)<sub>2</sub> precipitation.

<sup>19</sup>In the case of a little amount of precipitation, leave the solution over night.

(6) After the paper becomes ash by low temperature heating<sup>\*20</sup>, ignite the crucible at 800 °C for 10 minutes. Leave the crucible in a desiccator for cooling. Transfer the BaSO<sub>4</sub> precipitate into a weighing bottle. Then, weigh the weight (w g) of the precipitate.

Note: System diagram below is referred as a flow chart.

#### V-4. Calculation

$$\text{Total S (\%)} = (0.1374 * w/W) * 100$$

$$\text{SO}_3 (\%) = (0.3430 * w/W) * 100$$

## VI. FLUORINE

### VI-1. Summary

Powdered sample is mixed with V<sub>2</sub>O<sub>5</sub> which is a catalyzer for pyrohydrolysis. Under the controlled furnace temperature, the flow rate of carrier gas (air) and steam, fluorine in the sample is evaporated and brought into a bottle containing alkali solution. The solution absorbs fluorine. The pH is adjusted and the color produced by Alfusone is measured spectrophotometrically.

### VI-2. Apparatus

The outline of apparatus is shown in Figure 1.

### VI-3. Reagents

- (1) Vanadium pentoxide
- (2) Sodium hydroxide solution (0.5 %)
- (3) Hydrochloric acid (1+50)
- (4) PP indicator: A 0.1g of phenolphthalein is dissolved into 90 ml of ethanol (95 %). Then, the solution is made up to 100 ml by water.
- (5) Alfusone solution (5 %): A 5g of Alfusone is dissolved by 100 ml of water. The solution should be prepared fresh every time.
- (6) Acetone
- (7) Fluorine standard solution (1.0 mgF/ml): NaF is ignited at 500 °C. The process is repeated till obtaining a constant weight. Then, exact 2.210g of the reagent is weighed and dissolved in water. After making the solution to exact 1000 ml, it is preserved in a polyethylene bottle.

### VI-4. Analytical procedure

(1) Stabilize the apparatus under the conditions that temperature of electric furnace (9 in Figure 1) is 950 °C, temperature of water in the flask (3) is 90 ~ 95 °C and the flow rate of air is 200 ~ 500 ml/min.

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<sup>\*20</sup> High temperature heating at first stage may cause the reduction of BaSO<sub>4</sub> resulting low value of sulfur determination.

(2) Weigh 0.5 g of  $V_2O_5$  on the paraffin powder paper. Weigh 0.1 g (W g)<sup>\*21</sup> of sample precisely on the same paper. Mix them well and spread the sample evenly on a quartz boat.

(3) Fill 50 ml of water, 5 ml of NaOH solution (0.5 %) and 2 drops of PP indicator into the polyethylene bottle (12) connected to the quartz discharge tube (11). The bottle is cooled by ice pieces

(4) Insert the quartz boat including the sample into the center position of the electric furnace. Reconnect immediately the reaction tube (8) with the tube (5) introducing steam and air. Ignite the sample for 20 minutes under the optimum conditions<sup>\*22</sup>

(5) Remove the polyethylene bottle and add drop by drop HCl (1+50) until slightly pink color (pH  $\approx$  8)<sup>\*23</sup> is obtained in the bottle. Then, transfer the solution to a measuring flask (100 ml) and make the volume of solution exact 100 ml with water. This solution is designated to be the sample solution.

(6) Aliquot precise 1 ml (v/100)<sup>\*21</sup> of the sample solution into another measuring flask (50 ml). Add precise 5.0 ml of Alfusone solution (5 %) and 10 ml of acetone<sup>\*25</sup>. Then, fill water up to the mark of the flask and leave it for 90 minutes.

(7) Adjust the wavelength of spectrophotometer to 620 nm, then measure the absorbance of the colored sample solution referring to the absorbance of blank solution. Besides the sample solution, measure the absorbance of the standard series solutions which are prepared by adding 0.0, 0.01, 0.03 and 0.05 mg of F standard solution to the blank solution, respectively, and treating them by the same procedure as sample solution. Using a calibration curve made by the standard series, the concentration (C mg) of F in the sample can be determined.

Note: System diagram below is referred as a flow chart.

## VI-5. Calculation

$$F (\%) = [C/1000/(v/100)/V] \times 100$$

## VII. CHLORINE

### VII-1. Summary

Powdered sample is fused with  $Na_2CO_3$  and then Cl is extracted by warm water. Residue is separated using a glass filter. The filtrate and washing water are mixed and made up to a constant volume after neutralization with  $HNO_3$ . A part of the sample solution is aliquoted and added ferric ammonium sulfate and mercury (II) thiocyanate. The color obtained by the reaction of Cl with these reagents is measured spectrophotometrically.

<sup>\*21</sup> In the case of rock sample analysis, 0.25g of the sample should be weighed

<sup>\*22</sup> If the color of the solution in the bottle (12) disappears during the ignition, then add some more NaOH (0.5 %) to the bottle

<sup>\*23</sup> If the solution becomes acidic, the glass ware in use may be attacked by fluorine

<sup>\*24</sup> In the case of rock sample, 5 ml of the solution should be aliquoted.

<sup>\*25</sup> As the temperature of the solution will increase by the addition, make the solution to 50 ml after cooling it

## VII-2. Reagents

- (1) Sodium carbonate
- (2) Nitric acid (1+1.5)
- (3) Ethyl alcohol (95 %)
- (4) Ferric ammonium sulfate solution: A 60g of  $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  is dissolved by 1000 ml of  $\text{HNO}_3$  (1+1.5).
- (5) Mercury(II) thiocyanate alcohol solution: A 1.5g of  $\text{Hg}(\text{SCN})_2$  is dissolved by 500 ml of ethyl alcohol (95 %).
- (6) Chlorine standard solution (0.01 mgCl/ml): The Cl standard stock solution (1.0 mgCl/ml, refer Appendix I-3-2 for preparation) is diluted precisely 100 times by water.

## VII-3. Analytical procedure

(1) Weigh 0.5g (W g)<sup>\*26</sup> of sample precisely into a Pt crucible (30 ml). Add exact 3.00g of  $\text{Na}_2\text{CO}_3$  to the crucible and fuse them by heating for 30 minutes. Pour the fused sample just before solidification from the crucible into the dent of a Pt lid<sup>\*27</sup> and leave it for cooling.

(2) Transfer the solidified sample on the lid into an agate mortar. To the crucible, add 15 ml of water for dissolving the residual fused sample and transfer the solution into the agate mortar. With special care to flying off of the sample, crush the solidified sample by the agate pestle. Wash down the suspended solution from the mortar into a beaker (50 ml). Cover the beaker with a watch glass and heat it for dissolving soluble Cl.

(3) After cooling, separate the insoluble residue with suction filtration using a glass filter (G 4)<sup>\*28</sup>. Wash the residue with a small amount of water<sup>\*29</sup>. Collect the filtrate and washing water into another beaker (50 ml). Add 9.5 ml of  $\text{HNO}_3$  (1+1.5) to neutralize the solution. Then, transfer the solution into a measuring flask (50 ml) and make the volume of the solution exact 50 ml with water.

(4) Aliquot exact 20 ml of the solution into a color comparison glass tube (30 ml) with cap. Add precisely 4.0 ml of ferric ammonium sulfate -  $\text{HNO}_3$  solution and 2.0 ml of mercury (II) thiocyanate alcohol solution and mix the solution well.

(5) Leave the tube for 15 minutes, so that the color becomes to stabilize. Then, measure absorption at the wavelength of 460 nm in comparison with those of water.

(6) Aliquot 0.0, 3.0, 5.0, 7.0 and 10.0 ml of Cl standard solution (0.01 mg/ml) into the respective glass tubes (30 ml) and dilute precisely to 20 ml with water. Follow the procedures of (4) and (5) above. Using the results of measurement for the standard solutions, make a calibration curve from which the concentration (C mg) of Cl in the sample can be obtained.

Note: System diagram below is referred as a flow chart.

## VII-4. Calculation

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<sup>\*26</sup> The amount of sample depends on Cl content of the sample. Less than 0.25mg Cl in 50 ml of sample solution is recommended.

<sup>\*27</sup> The fused sample should solidify in a sphere shape.

<sup>\*28</sup> This indicates mesh size of glass filter.

<sup>\*29</sup> Total volume of the filtrate should be less than 30 ml.

$$CI (\%) = [C/1000/(20/50)/W]*100$$

### VIII. MOISTURE AND COMBINED WATER

The same procedures as V and VI in the silicate rock analysis can be adopted.

### IX. CARBON DIOXIDE

The same procedures as V in the carbonate rock analysis can be adopted.

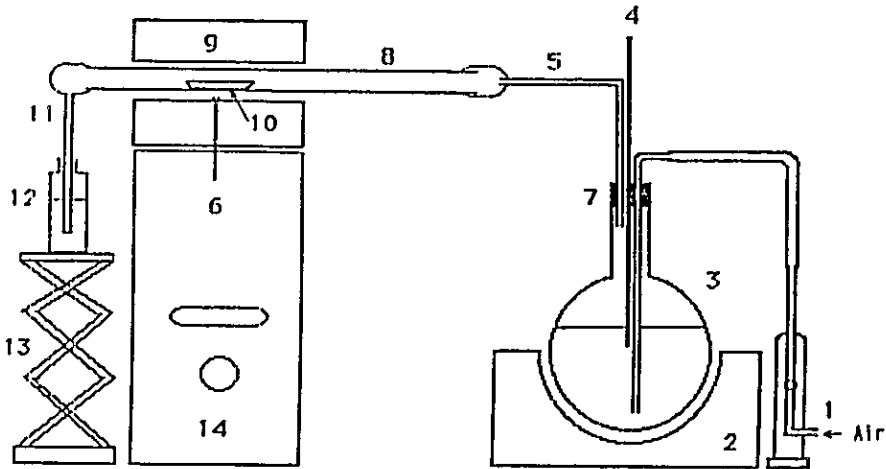
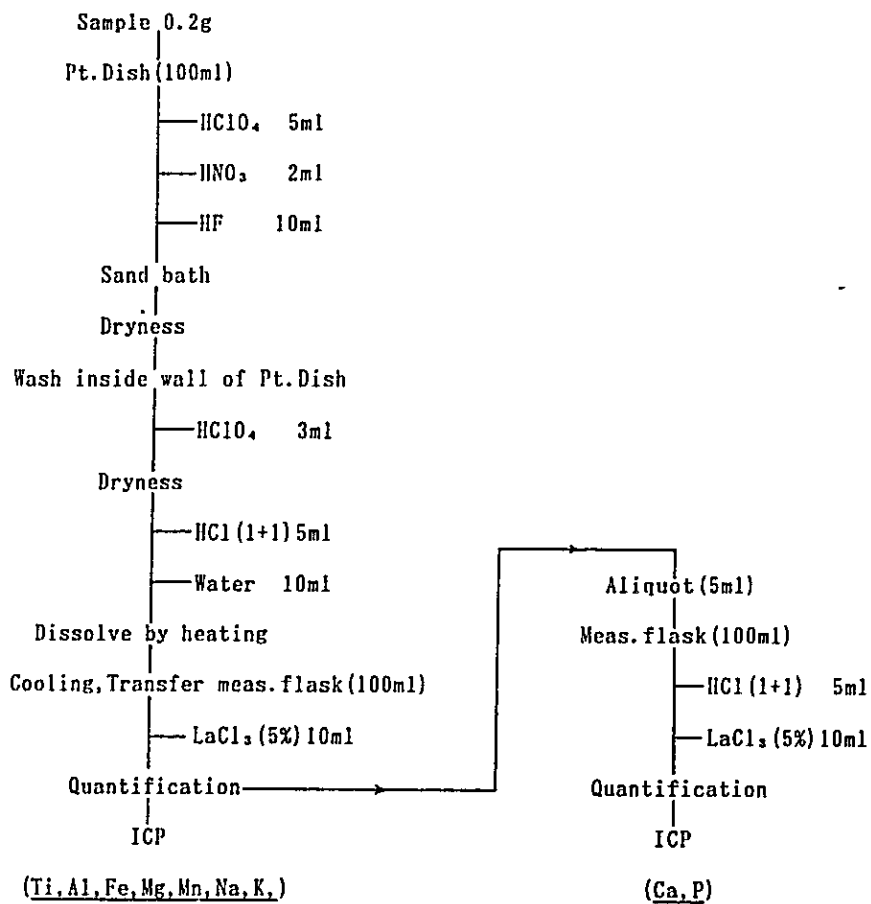


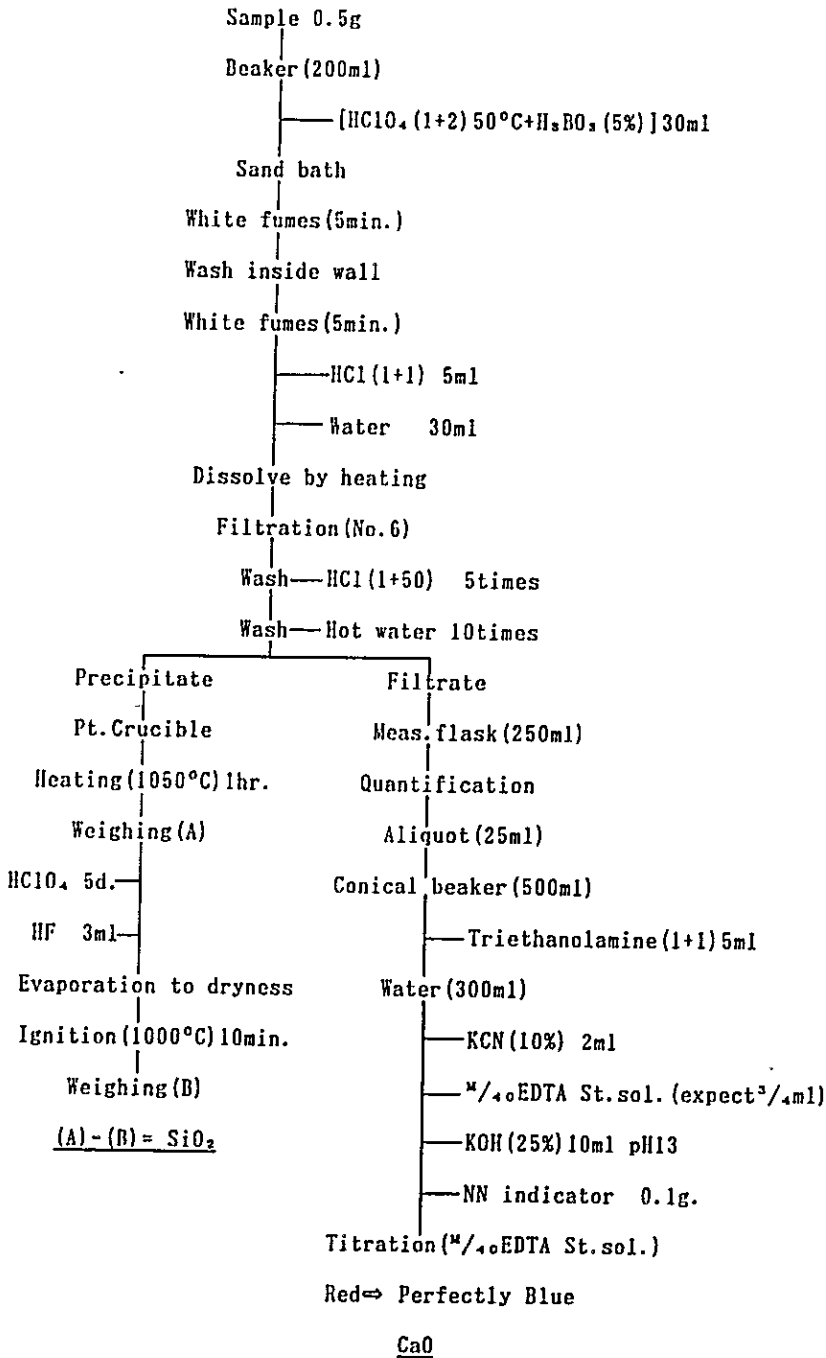
Figure 1. The design of pyrohydrolysis apparatus

- ① flowmeter, ② flask heater, ③ flask for generating steam
- ④ thermometer, ⑤ quartz tube introduction for steam and air
- ⑥ thermocouple, ⑦ silicon plug, ⑧ quartz reaction tube
- ⑨ tube furnace, ⑩ quartz boat, ⑪ quartz discharge tube
- ⑫ polyethylene bottle, ⑬ labo-jack, ⑭ furnace control

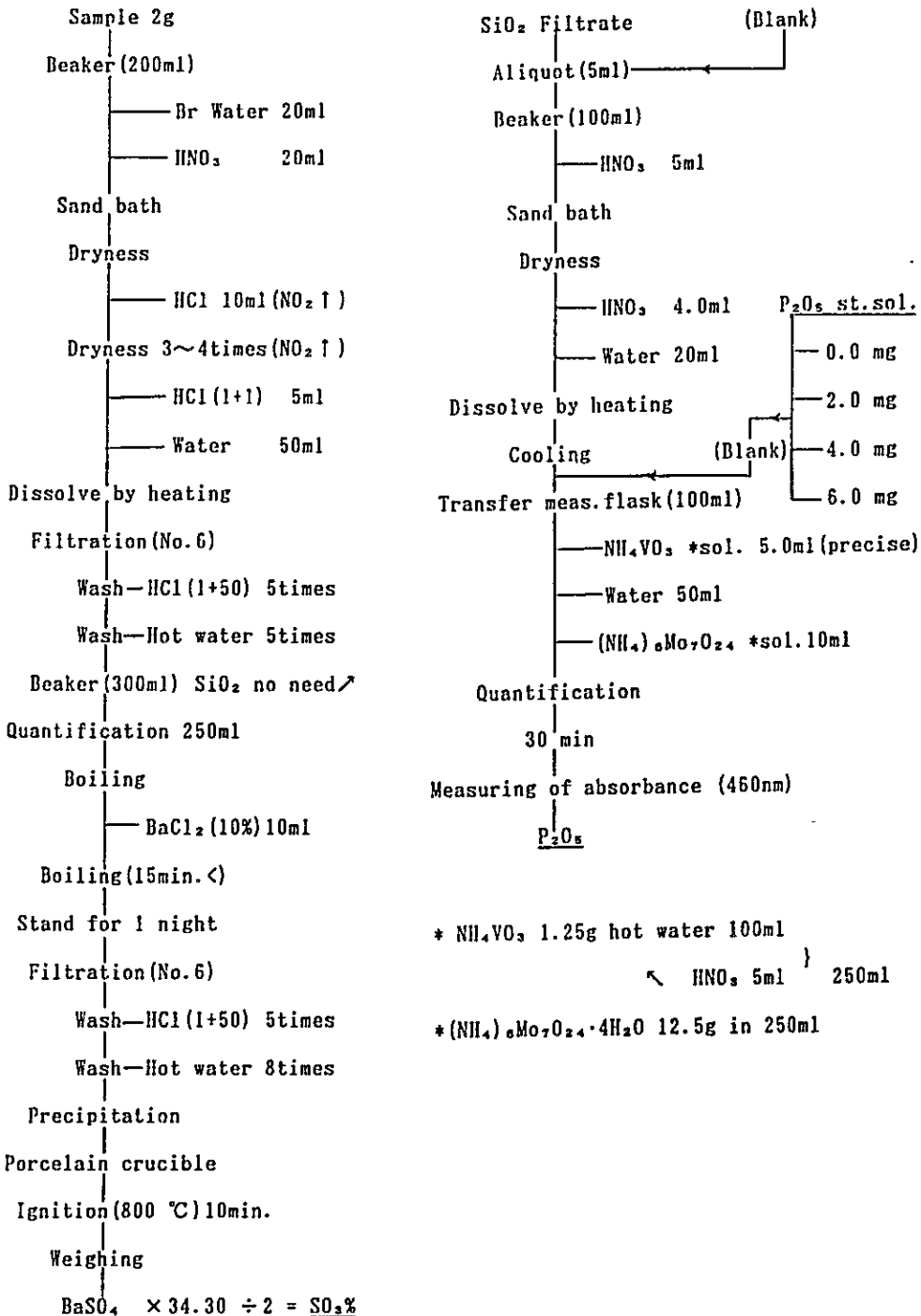
System Diagram of Phosphate ore Analysis (Ti, Al, Fe, Mg, Mn, Ca, Na, K, P)



System Diagram of Phosphate ore Analysis ( $\text{SiO}_2$ ,  $\text{CaO}$ )

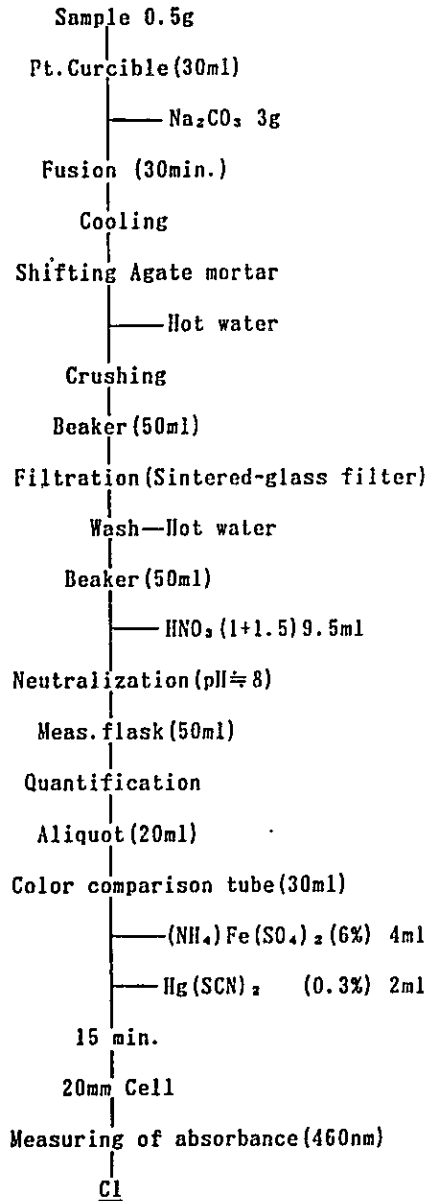
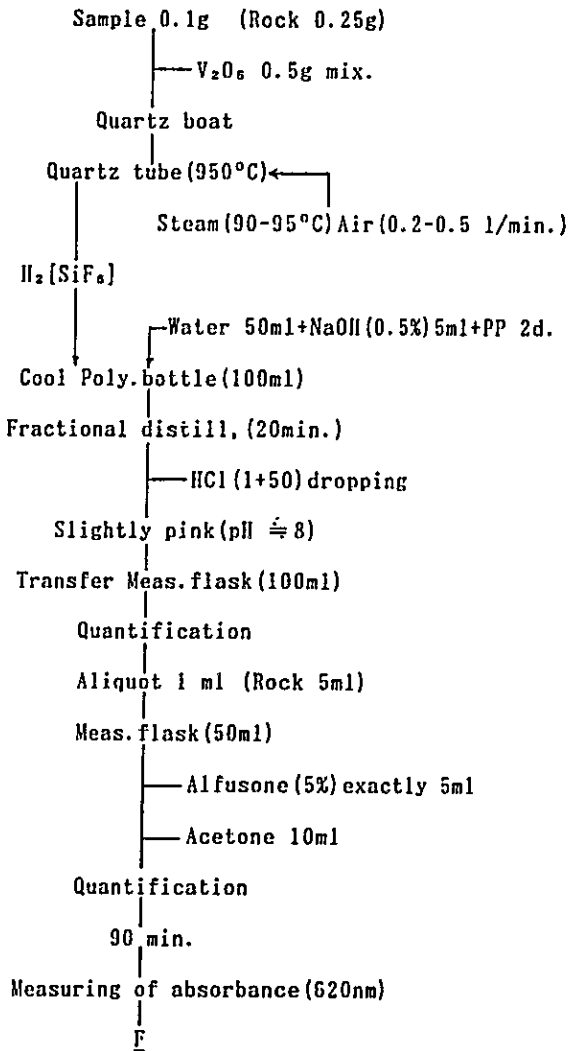


System Diagram of Phosphate ore Analysis ( $\text{SO}_3, \text{P}_2\text{O}_5$ )





System Diagram of Phosphate ore Analysis (F,C1)



## Recommended Analytical Method for Carbonate Rock Samples

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### I. SILICON DIOXIDE

#### I-1. Summary

The powdered sample is decomposed with hydrochloric acid and perchloric acid. After white fume ceases to evolve, the soluble matter is dissolved by hydrochloric acid. The residue in the solution is separated by filtration and then it is ignited. After cooling, the residue is weighed. Then, hydrofluoric acid is added to evaporate silicon dioxide. Again, the residue is ignited and weighed after cooling. Silicon dioxide content can be calculated from the difference of the weight before and after hydrofluoric acid digestion.

#### I-2. Reagents

- (1) Hydrochloric acid (1+1) and (1+50)
- (2) Perchloric acid
- (3) Hydrofluoric acid (50%<)

#### I-3. Analytical Procedure

(1) Weigh 0.5g (W g) of sample correctly into a beaker (200 ml). After moistening the sample with small amount of water, cover the beaker with a watch glass and add slowly 10 ml of HCl (1+1). After disappearance of bubbles, add 10 ml of HClO<sub>4</sub> and heat the solution in the beaker on a sand bath.

(2) Remove the watch glass and continue the heating of the beaker up to thick white fumes. Again cover the beaker with the watch glass<sup>\*1</sup>, heat for 10 minutes, then leave it for cooling.

(3) Add 5 ml of HCl (1+1) and 30 ml of water. By heating, dissolve the soluble matter, then filtrate the residue with a filter (No.6). Scrub the inside wall of the beaker with a policeman to remove the residue adhered and wash it down into the filter paper.

(4) Wash the residue 5 times by warm HCl (1+50) and 10 times<sup>\*2</sup> by warm water. All the filtrate is collected by a measuring flask (250 ml), which is made to a constant volume by water and stored for determining Ca and Mg (solution C).

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<sup>\*1</sup> If the beaker becomes to dry at this stage, some SiO<sub>2</sub> will adhere to the wall of beaker resulting low value in SiO<sub>2</sub> content.

<sup>\*2</sup> If the washing by water is inadequate, explosion may occur during ashing of the filter paper due to remaining HClO<sub>4</sub>.

(5) Transfer the residue together with the filter paper into a Pt crucible (30 ml), then, heat the crucible at low temperature until the filter paper is burnt to ashes. After that, ignite the crucible at 1000 ~ 1050°C for one hour, then leave it in a desiccator for cooling. After cooling, weigh the crucible and again ignite it for 20 minutes. Again weigh the crucible ( $w_1$  g)<sup>\*3</sup>.

(6) Moisten the impure SiO<sub>2</sub> by water, add 3 drops of HClO<sub>4</sub> and 5 ml of HF, and then heat it on a sand bath up to complete dryness<sup>\*4</sup>.

(7) After dry up, ignite the crucible at 1000 ~ 1050°C for 10 minutes and then leave it in a desiccator for cooling. After cooling weigh the crucible ( $w_2$  g).

Note: System diagram below is referred as a flow chart.

#### I-4. Calculation

$$\text{SiO}_2 (\%) = [(w_1 - w_2)/W] * 100$$

## II. CALCIUM OXIDE

### II-1 Summary

A part of the solution C of I-3-(4) is allocated to determine CaO. The masking reagent and KOH solution are added. After adjusting pH to 13 so that the interfering elements are masked, Ca is determined by the titration with M/40 EDTA standard solution using NN indicator.

### II-2. Reagents

- (1) Triethanolamine (1+1)
- (2) Potassium cyanide (10%)
- (3) Potassium hydroxide (25%)
- (4) NN indicator (refer. Appendix 1-3-2-Table 4-(vi) for preparation)
- (5) XO indicator (refer. Appendix 1-3-2-Table 4-(vi) for preparation)
- (6) M/40 EDTA standard solution (refer. Appendix 1-3-1-(3) for preparation)
- (7) M/40 Zinc standard solution (refer. Appendix 1-3-1-(3) for preparation)
- (8) Hexamine

### II-3. Analytical Procedure

(1) Aliquot 25 ml ( $v$  ml) of the solution C of I-3-(4) ( $250/W$  g) into a beaker (500 ml). Add 5 ml of Triethanolamine (1+1) and make it around 200 ~ 300 ml<sup>\*5</sup> with water.

(2) Add about 2 ml of KCN (10 %) solution and 8 ml of KOH (25 %) solution, so that the sample solution is adjusted to pH 13<sup>\*6</sup>.

<sup>\*3</sup> Repeat the procedures of ignition and weighing until the difference of weight is less than 0.5 mg.

<sup>\*4</sup> By this procedure both SiO<sub>2</sub> and HClO<sub>4</sub> are expelled.

<sup>\*5</sup> In order to avoid the adsorption of Ca ion to Mg(OH)<sub>2</sub> precipitate, the volume of the solution should be 200 ml for limestone sample and 300 ml for dolomite sample.

<sup>\*6</sup> After addition of 8 ml of KOH (25%) solution, the pH of the solution becomes 13 and Mg(OH)<sub>2</sub> is precipitated completely.

(3) Add about 0.05 ~ 0.1g of NN indicator<sup>\*7</sup>, then titrate by M/40 EDTA standard solution<sup>\*8</sup>. At the end point (V1 ml), color of the solution will change from red to complete blue.

(4) Aliquot precisely 20 ml (v1 ml) of M/40 Zn standard solution to a conical flask and add 5g of Hexamine<sup>\*9</sup>. Using XO as an indicator, titrate the standard solution by M/40 EDTA standard solution. Around the end point the titration should be carried out slowly and mixing the solution well. At the end point (v2 ml), claret color of the solution will be changed to bright yellow. From this titration, determine the factor (f) of M/40 EDTA.

Note: System diagram below is referred as a flow chart.

## II-5. Calculation

$$\text{factor of M/40 EDTA (f)} = v1/v2$$

$$\text{CaO (\%)} = [0.001402 * f * V1 * (250/W)/v] * 100$$

## III. MAGNESIUM OXIDE

### III-1. Summary

A part of the solution C of I-3-(4) is allocated to determine MgO. The masking reagent is added to mask the interfering elements. After adjusting pH to 10, sum of CaO and MgO can be titrated by M/40 EDTA standard solution using BT indicator. The MgO content is determined by subtraction of CaO content from the sum.

### III-2. Reagents

- (1) Hydroxylamine hydrochloride (10 %)
- (2) Triethanolamine (1+1)
- (3) Potassium cyanide (10 %)
- (4) Ammonium chloride - Ammonia water solution (pH 10 buffer solution); 70g of NH<sub>4</sub>Cl and 570 ml (ca. 500g) of NH<sub>4</sub>OH water (28 %) are mixed, then it is made to 1000 ml by water.
- (5) BT indicator (Eriochrome Black T)
- (6) XO indicator (Xylenol Orange)
- (7) M/40 EDTA standard solution (refer. Appendix 1-3-1-(3) for preparation)
- (8) M/40 Zinc standard solution (refer. Appendix 1-3-1-(3) for preparation)

### III-3. Analytical Procedure

<sup>\*7</sup> Because of the instability of coloring matter in the solution of NN indicator, it is diluted by K<sub>2</sub>SO<sub>4</sub>. Therefore, it is better to add the small amount of the indicator for easy recognition of color change.

<sup>\*8</sup> The factor of this standard will be determined in II-3-(4).

<sup>\*9</sup> By this addition the pH of the solution is adjusted to 6. However, care should be taken for impure reagents.

(1) Aliquot 25 ml (v ml) of the solution C of I-3-(4) (250/W g) precisely into a beaker (300 ml). Add about 5 ml of Hydroxylamine hydrochloride (10 %)\*<sup>10</sup> and mix the solution well.

(2) Add about 5 ml of triethanolamine (1+1)\*<sup>11</sup> and make it to about 100 ml by water. Add about 2 ml of KCN (10 %) solution and about 10 ml of NH<sub>4</sub>Cl-NH<sub>4</sub>OH water mixed solution\*<sup>12</sup>, so that the sample solution is adjusted to pH 10.

(3) Add 2 ~ 3 drops of BT indicator, then with continuous stirring titrate it by M/40 EDTA standard solution\*<sup>13</sup>. At the end point (V2 ml), color of the solution changes from red to complete blue.

(4) Aliquot precisely 20 ml (v1) of M/40 Zn standard solution into a conical flask and add 5g of Hexamine\*<sup>14</sup>. Using XO as an indicator, titrate the standard solution by M/40 EDTA standard solution. Around the end point the titration should be carried out slowly and mix the solution well. At the end point (v2), claret color of the solution changes to bright yellow. From this titration, determine the factor (f) of M/40 EDTA.

Note: System diagram below is referred as a flow chart.

#### III-4. Calculation

factor of M/40 EDTA (f) = v1/v2

MgO (%)<sup>\*15</sup> = [0.001008\*f\*(V2 - V1) (250/W)/v]\*100

### IV. OXIDES OF Fe, Al AND OTHERS

#### IV-1. Summary

The sample solution C of I-3-(4) is used for the determination of Fe and Al by AAS and ICP-AES. Also, Mg\*<sup>16</sup> in limestone can be determined by the same method.

#### IV-2. Reagents

(1) Mixed standard stock solution; 1g equivalent each of Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O and K<sub>2</sub>O, 0.1g equivalent each of MnO and P<sub>2</sub>O<sub>5</sub> and 2g equivalent of Al<sub>2</sub>O<sub>3</sub> are aliquoted precisely from each standard stock solution into a measuring flask of 1000 ml. After mixing well, 10 ml of HCl (1+1) is added and it is made exactly 1000 ml by water.

(2) Standard solution series for making the working curves of each elements; Exact 0.5 ml, 1 ml, 2 ml, 3 ml, 4 ml, and 5 ml of the mixed standard stock solution of

\*<sup>10</sup> This reagent acts as a reducing reagent and masks some interfering elements like Cu

\*<sup>11</sup> This reagent reacts with Fe, Al and Mn and forms stable chelate complex with them, so that they are masked

\*<sup>12</sup> A 10 ml of this buffer solution is enough to make solution pH 10, as such it isn't always necessary to measure pH.

\*<sup>13</sup> By this titration sum of Ca and Mg are determined.

\*<sup>14</sup> By this addition the pH of the solution is adjusted to 6. However, care should be taken for impure reagents.

\*<sup>15</sup> V1 in the formula means the volume of EDTA standard solution for Ca in II-3-(3)

\*<sup>16</sup> Magnesium content in limestone is generally low, so that the element can be correctly analyzed by this method.

IV-2-(1) are aliquoted into the respective 100 ml measuring flask. A 5 ml of HCl (1+1) is added to each flask, then the solution of each flask is made up to 100 ml precisely by water.

#### IV-3. Analytical Procedure

(1) Select optimum conditions of ICP-AES and AAS such as the wavelength, power input to the plasma, argon gas flow rate and the height in the tail flame for the elements to be analyzed.

(2) Using the standard solution series of IV-2-(2), make a correlation curve between concentration and intensity of emission<sup>\*17</sup> or absorption<sup>\*18</sup> for each element to be analyzed. From the correlation curve and the measuring intensity or absorbance of elements in the sample solution, calculate the concentration (C mg) of each element.

Note: System diagram below is referred as a flow chart.

#### IV-4. Calculation

$$\text{Element (\%)}^{*19} \text{ }^{*20} = (C/1000) \times (250/100/W) \times 100$$

### V. CARBON DIOXIDE

#### V-1. Summary

Using apparatus for carbon dioxide determination, carbonate in sample is decomposed by sulfuric acid. The evolved CO<sub>2</sub> gas is absorbed with sodium hydroxide-barium chloride solution. Then excess sodium hydroxide is titrated by N/10 HCl standard solution. From the result of the titration, content of carbon dioxide can be calculated

#### V-2. Apparatus

The apparatus is shown in Figure 3, in which

- (A, J) Rubber stopper
- (B) Sample decomposition flask
- (C) Spherical cooling device
- (D) Gas absorption flask
- (E, F) Rubber tube
- (G) Glass tube
- (H) Pinchcock
- (I) Insulation plate
- (K) Burette

#### V-3. Reagents

(1) Barium chloride solution; BaCl<sub>2</sub> · 2H<sub>2</sub>O 50 g/l + PP indicator (0.2 %) 2 ml

<sup>\*17</sup> In the case of ICP-AES, the intensity of emission is measured.

<sup>\*18</sup> In the case of AAS, absorbance is measured.

<sup>\*19</sup> The mg unit of standard solution is converted to g unit

<sup>\*20</sup> W is the sampling amount of I-3-(1)

- (2) PP indicator (0.2 %) (phenolphthalein)
- (3) N/10 Sodium hydroxide standard solution (0.45 %); standardization is not required.
- (4) N/10 Hydrochloric acid standard solution, (refer Appendix 1-3-1-(1) for preparation).
- (5) N/10 Sodium carbonate standard solution; (refer Appendix 1-3-1-(1) for preparation).
- (6) Sulfuric acid (1+1)
- (7) Bubble stones for boiling

#### V-4. Weighing out amount of sample

CO <sub>2</sub> content (%)	Sample (g)	NaOH (ml)
<1.0	1.0	10.00
1.0 ~ 2.5	0.5	10.00
2.5 ~ 7.5	0.5	25.00
7.5 ~ 15.0	0.25	25.00
>15.0	0.1	25.00

#### V-5. Analytical procedure

(1) According to the table of V-4, weigh 0.1 ~ 1.0g (W g)<sup>\*21</sup> of sample precisely and put it into the sample decomposition flask (B in Figure 1)<sup>\*22</sup>. Set the rubber stopper (A in Figure 1) and hold the flask by a steel stand as seen in Figure 1.

(2) To the gas absorption flask (D in Figure 1), add 150 ml of BaCl<sub>2</sub> and 150 ml of water. Then, add suitable amount of N/10 NaOH according to table V-4. Immediately, put the spherical cooling device (C in Figure 1) and fix it using a spring.

(3) As seen in the Figure, connect the decomposition flask (B) to the cooling device (C) and the absorption flask (D). Then, open the pinchcock (H) and the stopper of the cooling device (C). Add 2 ml of H<sub>2</sub>SO<sub>4</sub> (1+1) to the decomposition flask (B), and immediately<sup>\*23</sup> after that close the flask completely by the rubber stopper (A)

(4) Shake the decomposition flask (B), so that sample and the acid are mixed well. Then, heat the flask (B) to the extent that the entrance of the cooling device (C) is not possible to touch by finger any more. After reaching that condition, continue gentle boiling<sup>\*24</sup> for 10 minutes.

(5) Immediately after heating is stopped, close the rubber tube (F) using a pinchcock (H) and then separate it from the glass tube (G). Close the stopper of the cooling device (C) also. Cool the absorption flask (D) being connected to the cooling device (C) up to room temperature.

(6) Keeping the connection between (C) and(D), shake them hard up and down for 2 minutes, and then open the pinchcock (H) and the stopper of cooling flask (C).

<sup>\*21</sup> CO<sub>2</sub> content can be estimated roughly by means of dropping HCl to the small amounts of the sample moistened by water previously

<sup>\*22</sup> It is better to put several particles of boiling bubble stone into the flask for preventing violent boiling.

<sup>\*23</sup> The flask must be closed quickly to avoid any CO<sub>2</sub> leakage

<sup>\*24</sup> Heating should be adjusted to obtain only one or two drops of condensed water flowing down the glass tube in a few second

After that, flow down the remaining solution in the spherical part of the cooling device (C) to the flask (D).

(7) Separate the device (C) from flask (D). Wash the inside of the device (C) 3 times by water, all of which is collected by the flask (D). Put a stirring bar for magnetic stirrer into the flask (D). Put the rubber stopper (J) and burette (K) to the flask (D). The end of the burette should be inserted deeply<sup>\*25</sup> into the flask.

(8) Switch on the magnetic stirrer. Titrate the solution with N/10 IICl standard solution using PP indicator during which red color will disappear at the end point (v1 ml).

(9) Blank test; full procedures without sample input should be carried out (v2).

Note: System diagram below is referred as a flow chart.

#### V-4. Calculation

$$\text{CO}_2 (\%) = [0.002201 * (v_1 - v_2) / W] * 100$$

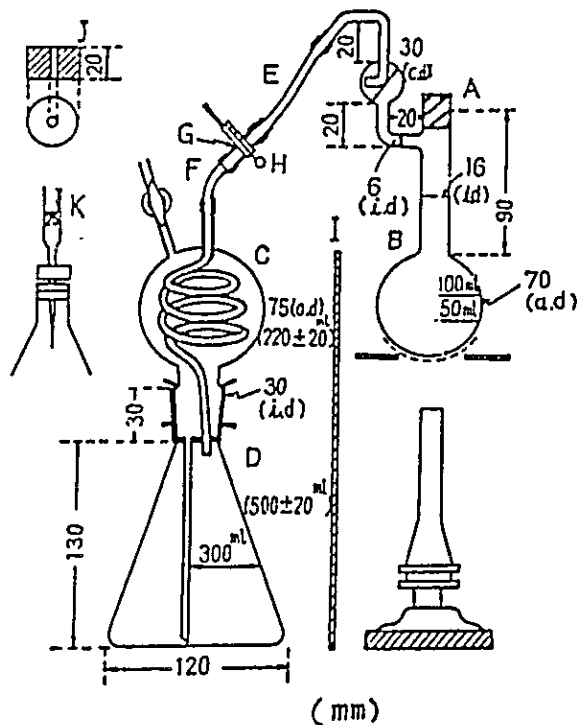
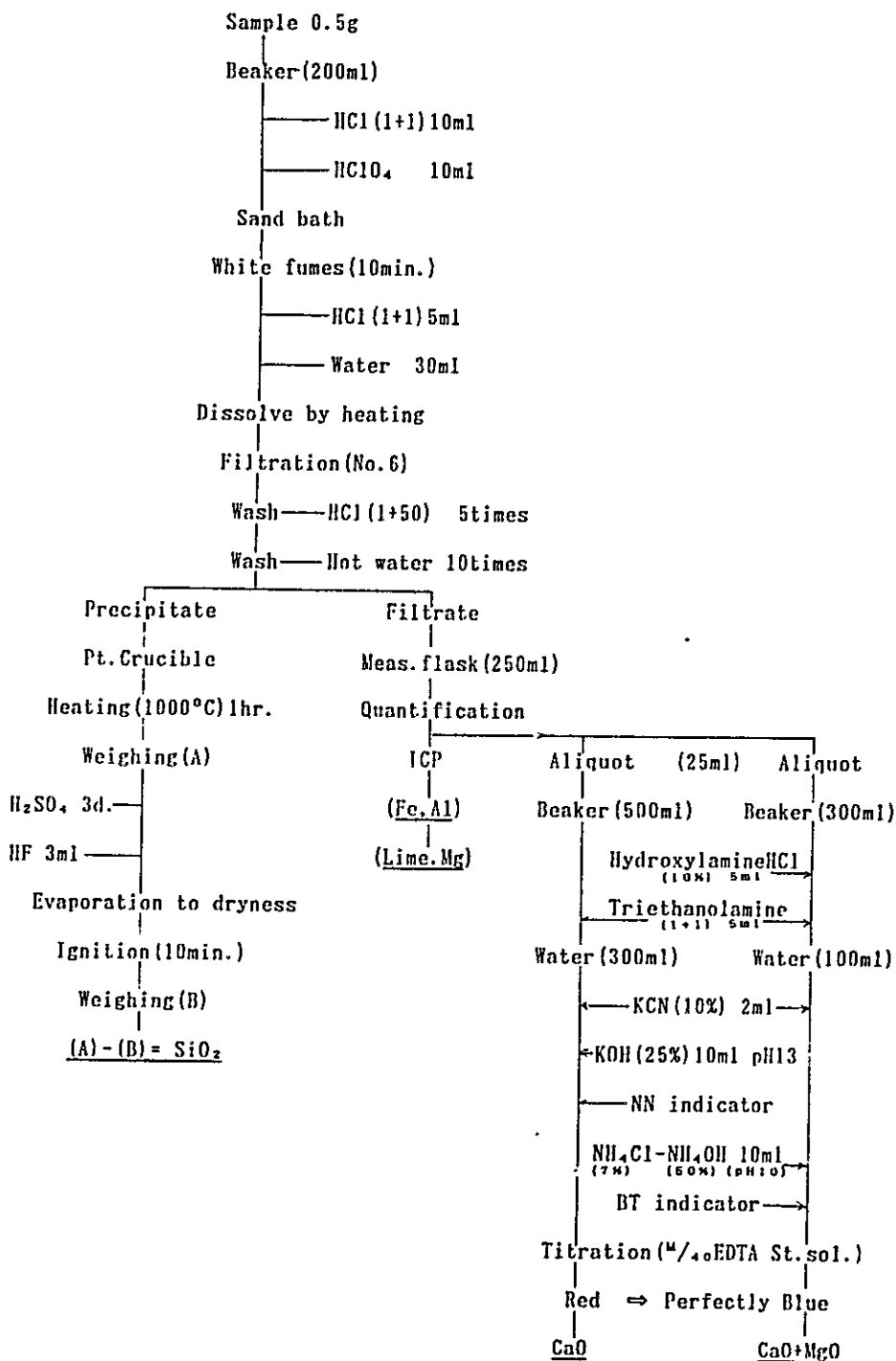


Figure 1. Apparatus for carbon dioxide determination

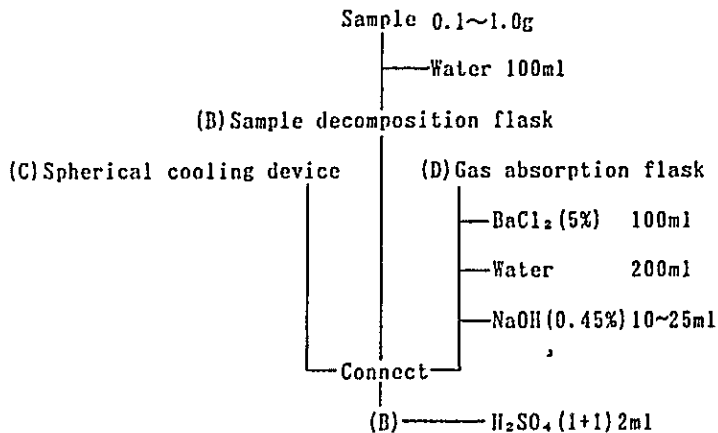
<sup>\*25</sup> As the rubber stopper (J) keeps the air closed, the air inside the flask must be leaked several times during the titration.



### System Diagram of Limestone and Dolomite Analysis



Method for Determination of CO<sub>2</sub> in Limestone and Dolomite



Dissolve by heating  
Boiling (8~10min.)

- Apparatus**
- (A, J) Rubber stopper
  - (B) Sample decomposition flask
  - (C) Spherical cooling device
  - (D) Gas absorption flask
  - (E, F) Rubber tube
  - (G) Glass tube
  - (H) Pinchcock
  - (I) Insulation plate
  - (K) Buret

- Reagents**
- (1) BaCl<sub>2</sub> sol.: BaCl<sub>2</sub> 2H<sub>2</sub>O 50g/l + PP (0.2%) 2ml
  - (2) <sup>N</sup>/<sub>10</sub> NaOH St.sol. (0.45%)
  - (3) <sup>N</sup>/<sub>10</sub> HCl St.sol.: HCl 8.4ml/l & <sup>N</sup>/<sub>10</sub> Na<sub>2</sub>CO<sub>3</sub> Standardization

CO<sub>2</sub>  
(C)  
(D)  
(H) Close  
(B) Separate (C, D)

Cooling  
Shaking (2~3min.)

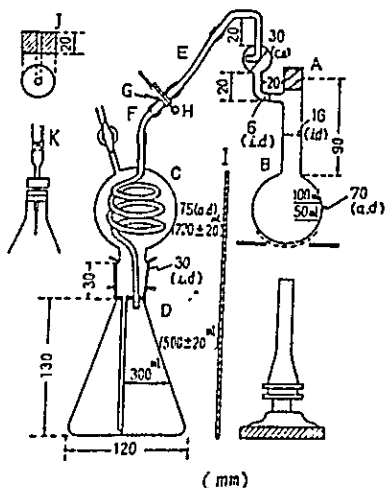
CO <sub>2</sub> %	Sample (g)	NaOH (ml)
1.0 >	1.0	10.00
1.0 ~ 2.5	0.5	10.00
2.5 ~ 7.5	0.5	25.00
7.5 ~ 15	0.25	25.00
15 <	0.1	25.00

Wash (3 times)

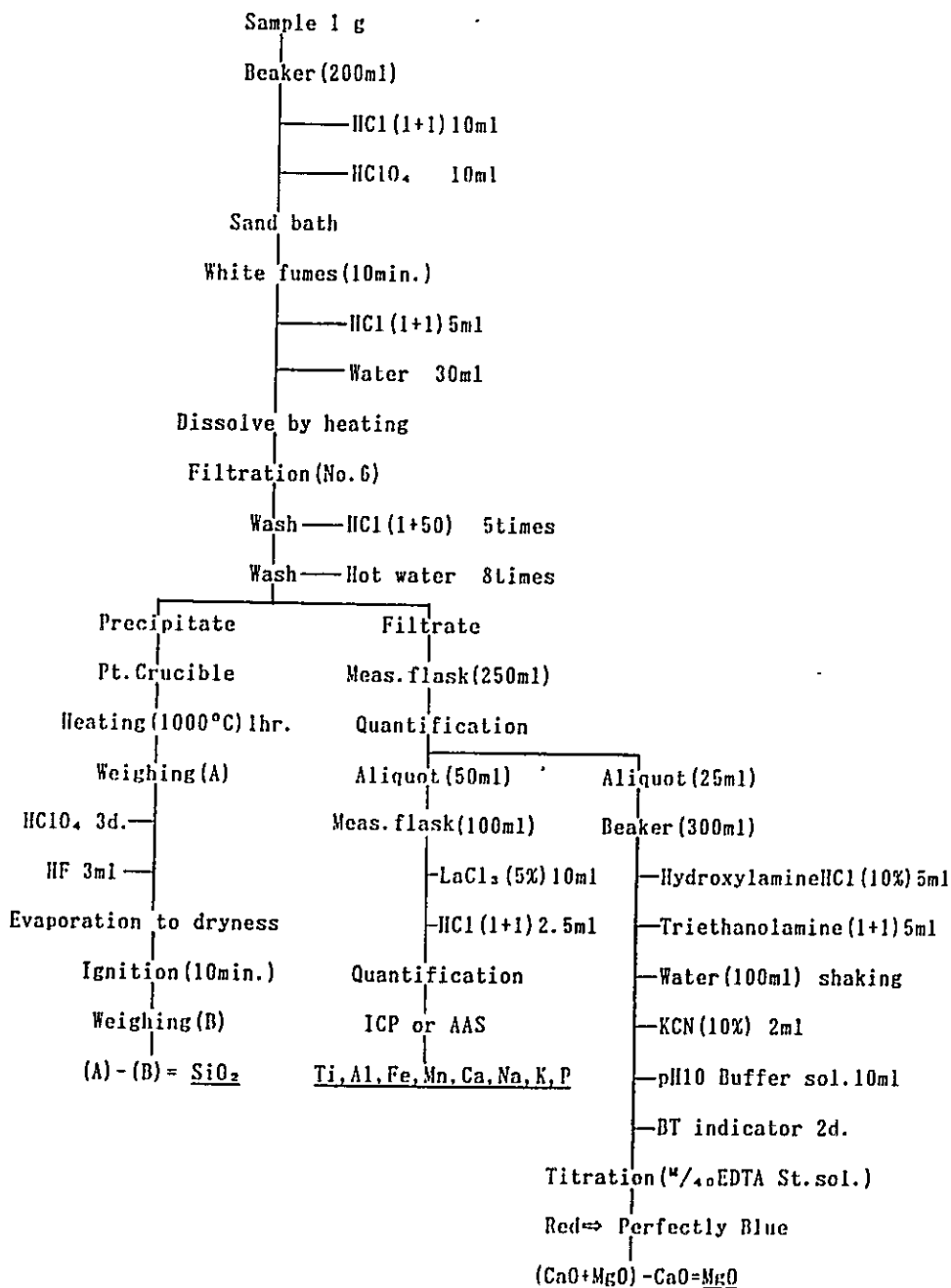
Connecting Buret  
Titrate (<sup>N</sup>/<sub>10</sub> HCl St.sol.)  
Pinkish ⇌ Colorless  
CO<sub>2</sub>

$$\text{CO}_2 (\%) = \frac{0.0022 \times f \times (v_1 - v_2)}{\text{sample (g)}} \times 100$$

where  $v_1$  : <sup>N</sup>/<sub>10</sub> HCl st.sol. of blank titration (ml)  
 $v_2$  : <sup>N</sup>/<sub>10</sub> HCl st.sol. of sample titration (ml)  
 $f$  : factor of <sup>N</sup>/<sub>10</sub> HCl st.sol.



## System Diagram of Magnesite Ore Analysis



## Analytical Method for Antimony and Arsenic in Geochemical Prospecting Samples

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### I. SUMMARY

In the presence of  $\text{KMnO}_4$  as an oxidant, the samples are decomposed by  $\text{HNO}_3$ ,  $\text{HClO}_4$  and  $\text{HF}$ . After drying up the solution, the residue is dissolved by  $\text{HCl}$ . Then,  $\text{KI}$  is added as an accelerator of reaction and successively the solution is made up to a constant volume.  $\text{Sb}$  and  $\text{As}$  in the solution are converted to the hydrides with  $\text{NaBH}_4$ , then determined by an atomic absorption spectrophotometer.

### II. APPARATUS

- (1) Atomic absorption spectrophotometer (AAS)
- (2) Hydride formation system (HFS)
- (3) T shape quartz cell
- (4) Platinum dish (100 ml)

### III. REAGENTS

- (1) Nitric acid
- (2) Perchloric acid
- (3) Hydrofluoric acid (Electronic grade chemical)
- (4) Hydrochloric acid (1+1) and (5 %)
- (5) Potassium permanganate solution (3 %)
- (6) Potassium iodide solution (50 %)
- (7) Sodium borohydride ( $\text{NaBH}_4$ ) solution (1 %); prepared by dissolving 1 g of  $\text{NaOH}$  and 10 g of  $\text{NaBH}_4$  with 1000 ml of water.
- (8) Antimony standard solution (1 mg/ml) and (10  $\mu\text{g/ml}$ ): A precise 1 ml of 1 mg/ml  $\text{Sb}$  stock solution is aliquoted into a measuring flask (100 ml), then 15 ml of  $\text{HCl}$  (1+1) is added and a constant volume (100 ml) by water is made. For the preparation of the standard stock solution (1 mg/ml), refer Appendix 1-3-2.
- (9) Arsenic standard solution (1 mg/ml) and (10  $\mu\text{g/ml}$ ): A precise 1 ml of 1 mg/ml  $\text{As}$  stock solution is aliquoted into a measuring flask (100 ml), then 15 ml of  $\text{HCl}$  (1+1) is added and a constant volume (100 ml) by water is made. For the preparation of the standard stock solution (1 mg/ml), refer Appendix 1-3-2.

#### IV. PROCEDURE

(1) Weigh 0.5 g (W g) of sample precisely and put it in a platinum dish (100 ml). First sample in a batch is sampled three times for standard addition method, and the solutions from this same sample may be numbered as No. 1a, 1b and 1c.

(2) Add 5 ml of  $\text{HNO}_3$ , 5 ml of  $\text{HClO}_4$  and 10 ml of HF. Mix them with a Pt wire and leave it for a few minutes. Add appropriate amount of  $\text{KMnO}_4$  solution (3 %)<sup>(1)</sup> and heat<sup>(2)</sup> it on a sand bath, so that the sample is dissolved without any loss of As and Sb.

(3) Heat continuously<sup>(3)</sup> and generate thick white fumes, so that silica is expelled completely, and then dry it up.

(4) After cooling, wash inside wall of the Pt dish with small amount of water. Add 2 ml of  $\text{HClO}_4$  and heat it again on the sand bath till slightly<sup>(4)</sup> dry up.

(5) After cooling, add 8 ml of HCl and 20 ml of water. Cover the dish with a watch glass and heat to dissolve the residue. Leave it for cooling. After cooling, transfer the solution into a measuring flask (100 ml) along with washing water.

(6) For standard addition method<sup>(5)</sup> sample No. 1a is assigned as an original. To the No. 1b and 1c solutions add 0.5  $\mu\text{g}$  and 1.0  $\mu\text{g}$  Sb respectively taken from the Sb standard stock solution (10  $\mu\text{g}/\text{ml}$ ). To all sample solutions including these three 10 ml of KI (50 %) solution is added and then they are made up to a constant volume (100 ml) with water, from which Sb is determined (solution A).

(7) A precise 10 ml of each sample solution (A) is aliquoted to another measuring flask (100 ml). The aliquot solution from the same solution assigned for standard addition method in (6) are again added 0.0  $\mu\text{g}$ , 1.0  $\mu\text{g}$  and 2.0  $\mu\text{g}$  As respectively taken from the As standard stock solution (10  $\mu\text{g}/\text{ml}$ ). All sample solutions including these three are added 9 ml of KI (50 %) solution and 15 ml of HCl (1+1), and then they are made up to a constant volume (100 ml) with water from which As is determined (solution B).

(8) Fill the Carrier bottle attached to the hydride generation equipment (HFS) with distilled water, similarly fill the HCl bottle with HCl (5 %) and the  $\text{NaBH}_4$  bottle with  $\text{NaBH}_4$  (1 %) solution. These bottles are connected correctly to the HFS with tubes.

(9) Set the sampling timer of HFS to 1.0 (60 sec.), the reaction timer to 0.5 (30 sec.), and argon gas flow rate to 50 ml/min. After confirmation<sup>(6)</sup> of all setting, turn the power switch ON.

(10) Set a quartz cell on the air-acetylene burner of AAS. Connect the cell to the HFS using a support clamp lever and rubber tube through which metal hydrides will be sent to the cell. Ignite the flame and heat the cell.

---

(1) Some As will evaporate easily, if the sample is decomposed under the condition of less oxidation.

(2) At first heat weakly, so that the decomposition of sample by HF is complete.

(3) If the pink color of the solution is disappears at this stage, supplement additional  $\text{KMnO}_4$  solution till the solution is stained pink.

(4) If the solution is strongly dried, both Sb and As evaporate.

(5) To avoid the error from the difference of liquid composition, the standard addition method is adopted.

(6) Before turning the power switch ON, argon gas should be run through the system. Otherwise, the gas flow meter will be invaded by water and make trouble.

(11) Set the analytical conditions of AAS for Sb such as a wavelength of 217.6 nm, standard addition measurement, calculation peak height and calculation time of 20 seconds. Then, turn the switch of AAS ON<sup>(7)</sup>.

(12) Insert the suction tube into the measuring flask of sample solution (A), then, push the start button for starting measurement. From the measuring data of absorbance<sup>(8)</sup>, determine Sb concentration ( $\mu\text{g}$ ).

(13) Set the analytical conditions of AAS for As; a wavelength of 197.2 nm, others are the same as those for Sb. From the measuring data of absorbance for sample solution (B), determine As concentration ( $\mu\text{g}$ ).

Note; System diagram below is referred as a flow chart.

## V. CALCULATION

$$\text{Sb (ppm)} = \text{Sb } (\mu\text{g}) / W$$

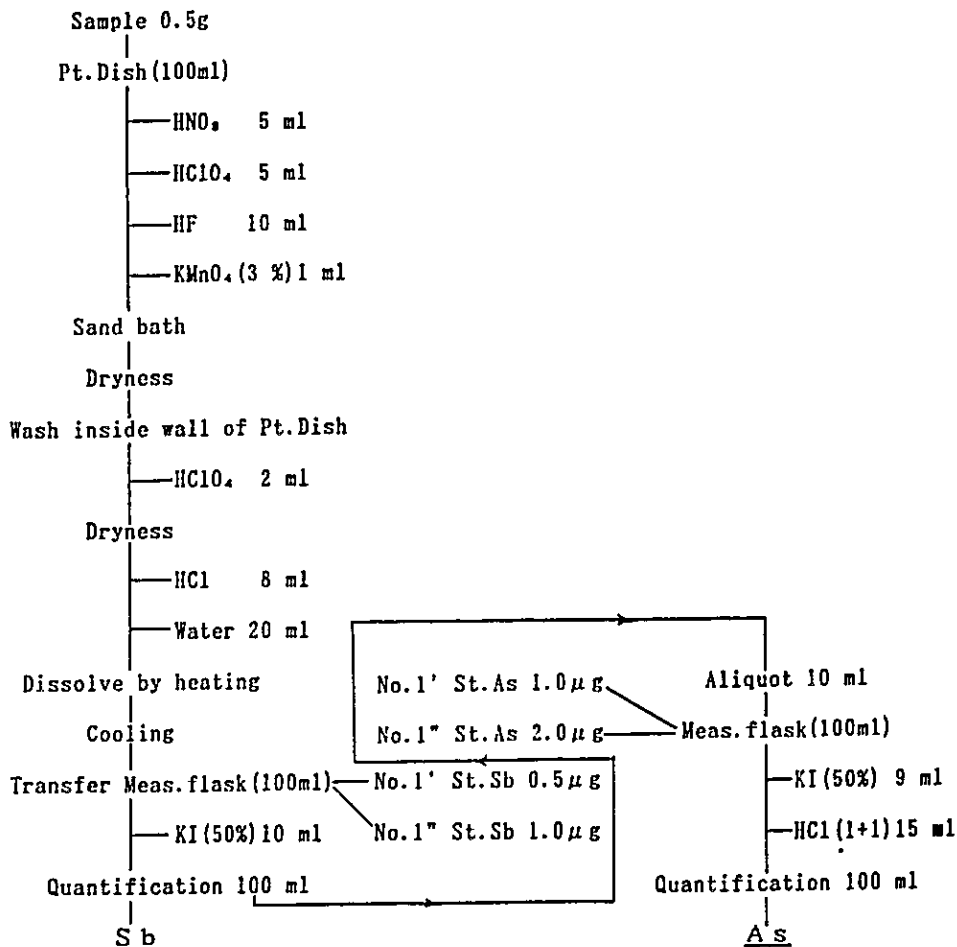
$$\text{As (ppm)} = \text{As } (\mu\text{g}) / W$$

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<sup>(7)</sup> After turning the switch ON, repeat the measurement 2 ~ 3 times for stabilizing the measurement system.

<sup>(8)</sup> At first, make the calibration curve using the data of the solution added with standard Sb solution.

### System Diagram of As, Sb Hydride Analysis



S b

Wavelength	217.6nm
Atomizer	Quartz cell
Flame	C <sub>2</sub> H <sub>2</sub> -Air
Measurement	Std. add.
Calculation	Peak height
Calc. time	20 sec.
Sampling time	60 sec.
Reaction time	30 sec.
Ar Flow	50 ml/min.

A s

Wavelength	197.2nm
Atomizer	Quartz cell
Flame	C <sub>2</sub> H <sub>2</sub> -Air
Measurement	Std. add.
Calculation	Peak height
Calc. time	20 sec.
Sampling time	60 sec.
Reaction time	30 sec.
Ar Flow	50 ml/min.

## Analytical Method for Mercury in Geochemical Prospecting Samples

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### I. SUMMARY

Powdered samples are decomposed by ignition with additives using a tube furnace. The released mercury vapour is trapped by gold as amalgam, so that dominant other vapours like carbon dioxide and water can be separated from the mercury. Then, the Au-Hg amalgam is heated. The atomized mercury released from the amalgam is transferred to an absorption cell. The amount of Hg is determined by flameless atomic absorption method.

### II. APPARATUS

- (1) Mercury detector, Nippon Instruments Model SP-3D (Figure 1): This consists of Sample Processing (SP), Mercury Atomizer Controller (MA), Mercury Detector (MD) and Others for a complete set of gold amalgam method.
- (2) Electric furnace: Temperature adjustable tube furnace.
- (3) Porcelain crucible (50 ml).
- (4) Sample boat (L 110 mm, W 15 mm, D 13 mm).

### III. REAGENTS

- (1) L-cysteine solution (0.001 %): A 5mg of L-cysteine is weighed into a measuring flask (500 ml) and 1 ml of HNO<sub>3</sub> is added to the flask. Then, the flask is filled up to the mark with water.
- (2) Hg standard stock solution (1000 ppm): An exact 0.1354g of HgCl<sub>2</sub> is weighed and put it into a measuring flask (100 ml). The flask is, then, filled upto the mark with L-cysteine solution (0.001 %). This stock solution can be preserved up to 6 months.
- (3) Hg standard solution (10 ppm): 1 ml of the stock solution [III-(2)] is aliquoted precisely to a measuring flask (100 ml) and is diluted 100 times with L-cysteine solution (0.001 %). This solution can be preserved upto one month.
- (4) Hg standard solution (50 ng): 0.5 ml of the stock solution [III-(2)] is aliquoted precisely to a measuring flask (100 ml) and the flask is filled upto the mark with L-cysteine solution (0.001 %). This solution can be preserved up to three weeks.
- (5) Additive B (active alumina): Before using the reagent, it should be ignited at 750 °C for 3 hours using a porcelain crucible, so that Hg in the reagent



- may be expelled. The reagent previously ignited can be used after one hour ignition at 750 °C and the ignition should be carried out every three hour.
- (6) Additive M (sodium carbonate plus calcium hydroxide): The reagent should be used after the same treatment as given to Additive B above.
  - (7) Standard pH 7 buffer solution (1+1): A 3.40g of  $\text{KH}_2\text{PO}_4$  and a 3.55g of  $\text{Na}_2\text{HPO}_4$  are dissolved by 1000 ml water. It is, then, further diluted to (1+1) with water.

#### IV. ANALYTICAL PROCEDURE

##### IV-1. Measuring conditions and calibration curve

(1) Add 20 ml<sup>\*1</sup> of standard pH 7 buffer solution (1+1) to the scrubbing bottle of SP (Scrubber in Figure 1). Turn ON the respective power switch of MA and MD. The power must be 100 ~ 110 V.

(2) Adjust the pressure of carrier gas (air) to 0.4 kg/cm<sup>2</sup>. Also, adjust the flow rate of the gas to 0.5 l/min for both burning side (left side flowmeter) and cell side (right side flowmeter).

(3) Turn up the leak-test switch on the backside of SP and shut off alternately<sup>\*2</sup> the gas flow at the exhaust exit of burning side and cell side by a finger. The respective flowmeter should indicate zero flow rate, so that no leak is confirmed.

(4) When the flowmeter suggests some leak of carrier gas, check each of the Teflon joint throughout the flowing system and tight the loose joint. After confirming the zero indication of both sides flowmeter, turn down the leak-test switch and run the apparatus in the steady conditions for more than 20 minutes, so that optics and heat system is stabilized.

(5) Take the reagents (Additive B and M) and the sample boat out of the electric furnace at 15 minutes before starting measurement, and leave them for cooling. Using alcohol, clean the spatula, the pincette (forceps) and the rod for inserting boat.

(6) Push the Mode 1 Key for calibration procedure (refer Figure 2) Input the range of measurement (in this case, 20 ng) from the Range Key on MD (refer Figure 3).

(7) Cover the floor of the sample boat with Additive B in thickness of 2 ~ 3 mm. Using the insertion rod, insert the boat into the fixed place of the tube Furnace. Then, close the entrance of the tube with the cap and push the Start Key of MA.

(8) After pushing the start button, IIG measuring procedure starts automatically and finishes with a sound of buzzer. The display of MD-1 shows like Figure 4. After finalizing the measurement, input the concentration of the added Hg (in this case, 0 for blank measurement) to the x1 position of the LCD from the numeric keys on MD-1 (see Figure 4). Then, push successively the Enter Key and Adopt Key of keyboard, resulting presentation and printing of the value y1<sup>\*3</sup> (for Enter Key and Adopt Key refer to Figure 3).

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<sup>\*1</sup> The height of the solution in the scrubbing bottle should be kept at the level of approximate 20 mm higher than the level of the air blow out mouth. The solution should be changed after every 30 measurement.

<sup>\*2</sup> It is not allowed to shut off both gas flows at the same time

<sup>\*3</sup> Because at the beginning of first measurement the result include contamination in the SP system, the blank procedure should be repeated.

(9) Take out the sample boat from the tube furnace. Prepare another boat covering the floor with Additive B in thickness of 2 ~ 3 mm and add 5 ng of Hg standard solution precisely using a micropipette. Proceed the same procedure as blank test above.

(10) Same procedure should be applied for 10 ng and 15 ng of Hg standard solution. All results of standard series are memorized in MA.

(11) After completion of standard solution, push the Menu button to end the calibration status. This will give the best fitted straight line for calibration (see Figure 5).

#### IV-2. Measurement of samples

(1) Cover the floor of a sample boat with Additive M in the thickness of 2 ~ 3 mm. Weigh sample powder of 0.5g (W g) precisely and spread it on the Additive M in the boat (refer Method 2 in Figure 6).

(2) Cover the sample in the boat with additional Additive M on which Additive B is spread in the thickness of 2 ~ 3 mm. Finally, spread again Additive M on the Additive B layer<sup>\*4</sup> (Figure 6).

(3) Push the Mode 2 key<sup>\*5</sup> of MA. Insert the prepared sample boat into the fixed place of the tube furnace of SP. Close the entrance of the tube with the cap and then press the start key.

(4) According to the program of MA, SP will proceed from Ready to Atomize, then, through Trans, Heat and Cool, will reach to Ready automatically. Finishing the measurement is informed by the sound of buzzer and the result of the Hg measurement is presented in the LCD of MA.

(5) Input sample No. and sample weight (W mg) to the LCD from keyboard. Push the Enter key and then Adopt key. Hg (ppb) will be calculated and printed automatically on the Printer recorder.

Note: System diagram below is referred as a flow chart.

### V. ANALYTICAL RESULTS FOR SOME STANDARD ROCKS

Some standard reference materials (SRM) issued from Geological Survey of Japan have been analyzed by this procedure. The results are summarized in Table 1 showing in very good agreement with the values found in a literature.

Table 1 Analytical results of mercury for some standard rock samples (in ppb).

SRM	RANGE	MEAN	OTHER VALUES <sup>*6</sup>
JG-1	18.9 - 22.0	20.48	19.0
JB-1	28.0 - 32.9	30.77	30.0
JA-1	10.7 - 16.0	13.45	15.0
JB-1a	5.0 - 7.26	6.47	5.30

<sup>\*4</sup> After finishing the preparation, the bottom side of the sample boat should be wiped off by a paper, so that contamination of the inside of tube furnace can be avoided.

<sup>\*5</sup> In the case of Mode 2, the furnace ignites at 350 °C for 4 minutes in the first step and at 700 °C for 6 minutes in the second step.

<sup>\*6</sup> Shigeru TERASHIMA, 1994, Geost. Newsl. vol. 18, 199-202

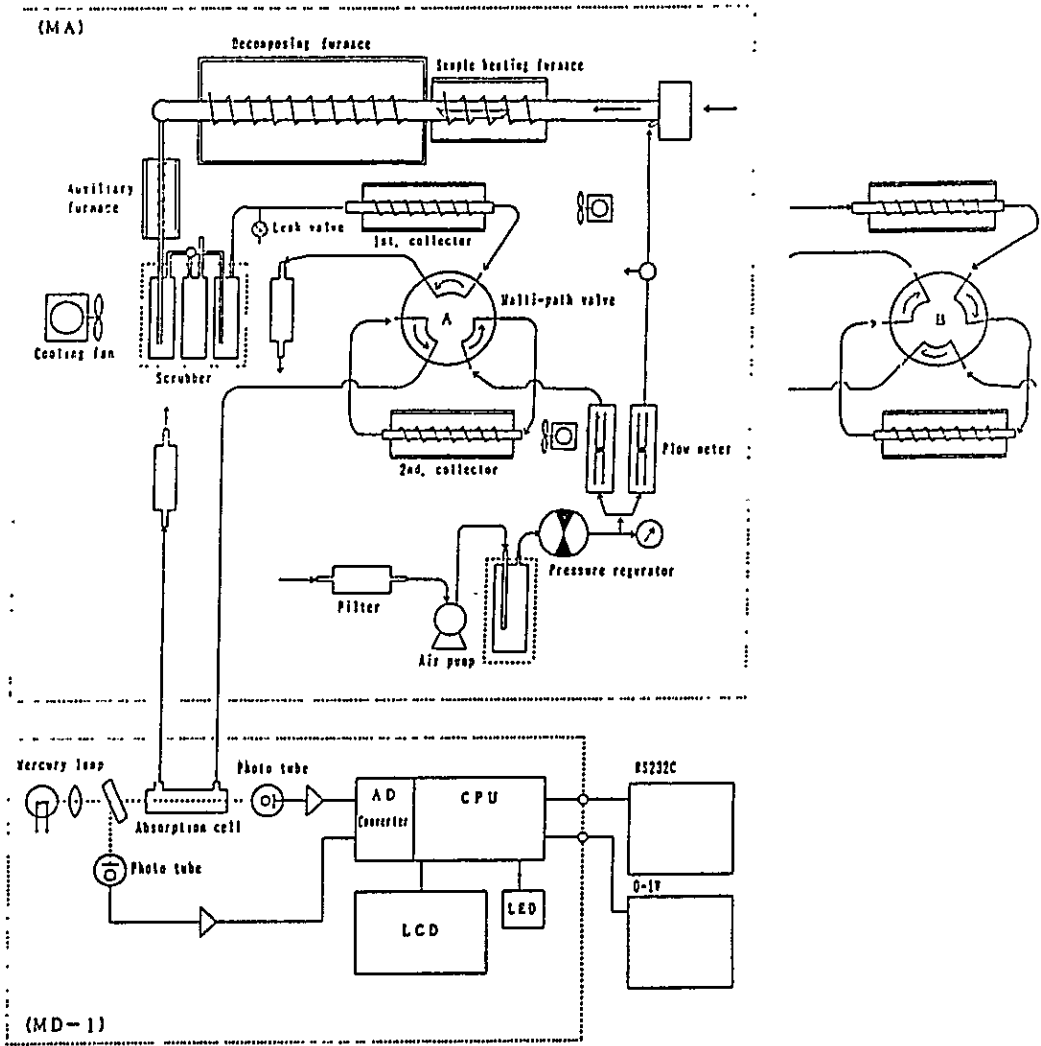


Figure 1. Schematic diagram of mercury analyzer

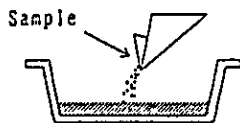
AT	RANGE	MODE	STATUS
SP	20	PEAK	CALIB
	x1 =		y1 = 10.6
	y = 1.000 x + 0.000		

Figure 4. LCD on MD-1 in Calibration Status waiting for the entry of x1 value.

AT	RANGE	MODE	STATUS
SP	20	PEAK	READY
	y = 1.060 x + 0.000		

Figure 5. LCD in Ready Status with best fitted straight line.

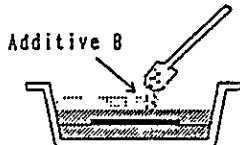
Additive Application method-2 (for solid/powder sample)



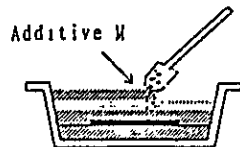
Spread a layer of additive M on the bottom of the sample boat. Weigh the solid/powder sample and place it onto the layer of additive M.



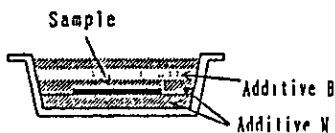
Put a layer of additive M over the sample.



Put a layer of additive B over the layer of additive M.



Finally, cover the layer of additive B with a layer of additive M.



Sectional view of a finished sample boat.

Figure 6 Additive Application method-2 (for solid/ powder sample).

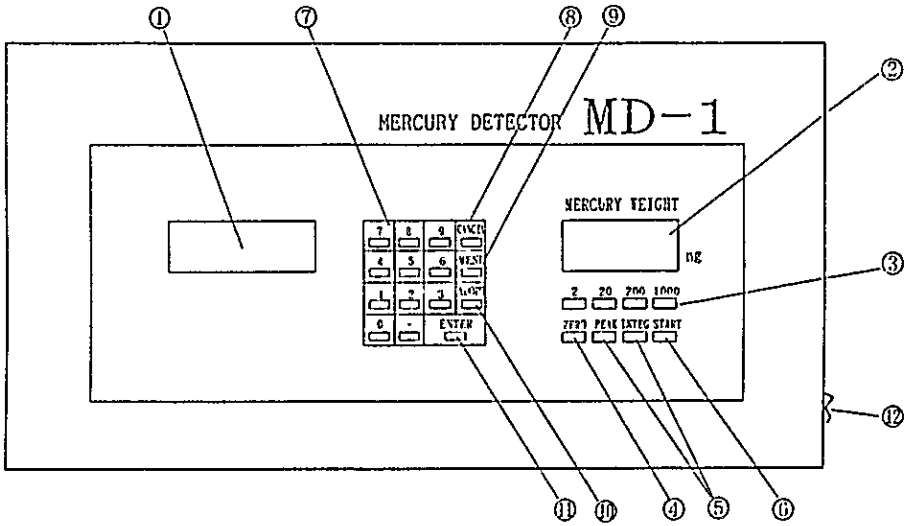


Figure 2. Schematic diagram of MD-1 Front Panel.

- ① LCD Display
- ② LED Display
- ③ RANGE Keys
- ④ ZERO Adjust Key
- ⑤ PEAK/INTEG Selector Key
- ⑥ START Key
- ⑦ Numeric Keys
- ⑧ CANCEL Key
- ⑨ MENU Key
- ⑩ ADOPT key
- ⑪ ENTER Key
- ⑫ POWER Switch

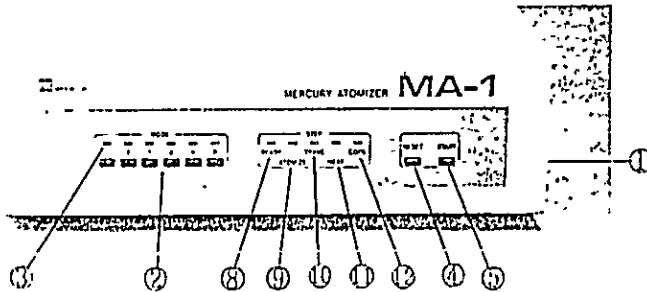
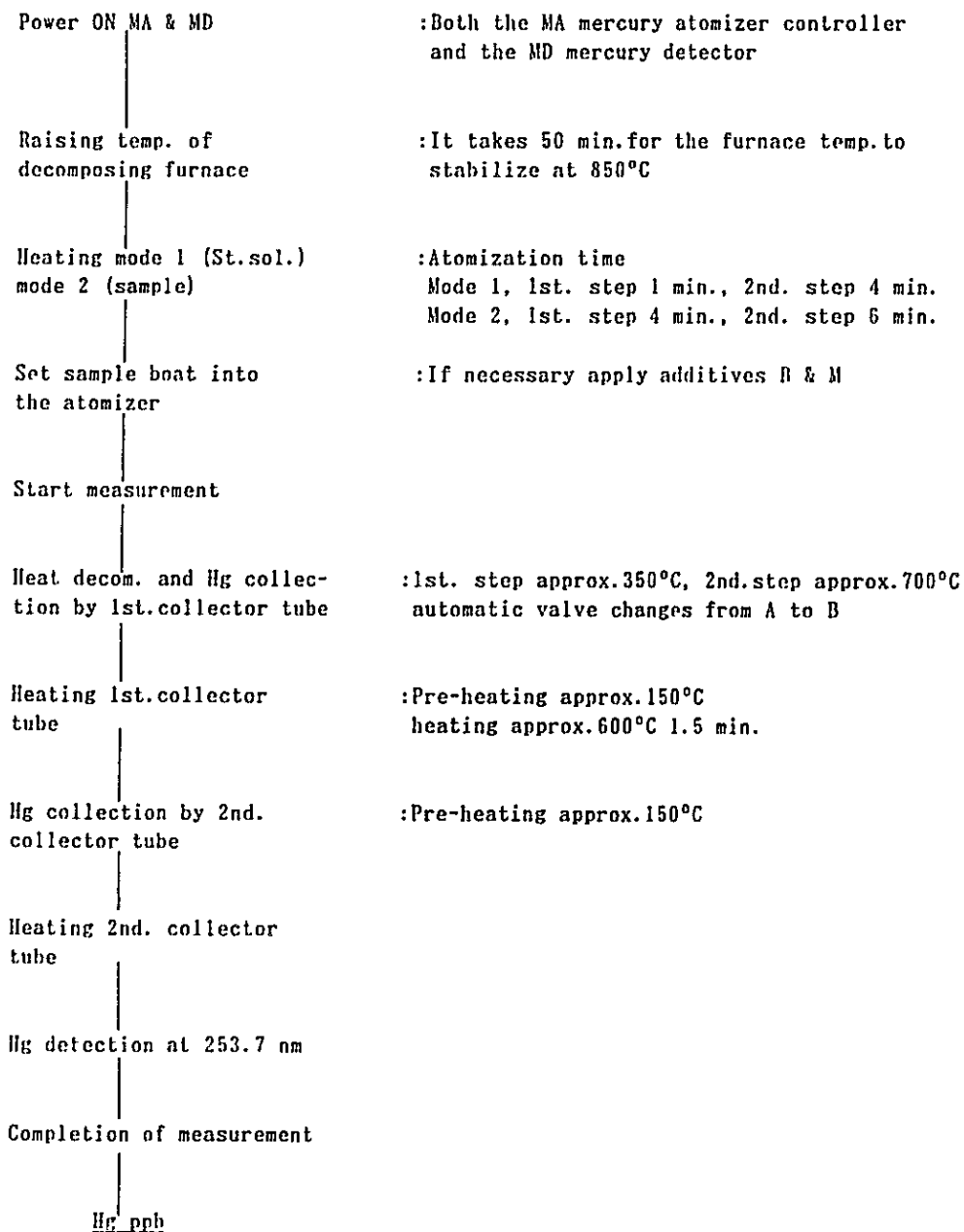


Figure 3. Schematic diagram of MA-1 Front Panel

- ① POWER Switch
- ② MODE Selector Keys
- ③ STEP Indicators
- ④ RESET Key
- ⑤ START Key
- ⑥ READY Indicator
- ⑦ ATOMIZE Indicator
- ⑧ TRANS Indicator
- ⑨ COOL Indicator

## System Diagram of Hg Measurement Procedure



## APPENDIX





## APPENDIX I

### 1. PREPARATION OF STANDARD SOLUTIONS

#### 1-1. Chemical reagents

Reagent being used for chemical analysis should be of the purest and highest grade. Table 1 shows some properties of liquid reagents which are used regularly for chemical analysis.

Table 1. Liquid reagents in common use  
(ca. means approximate)

reagent	sp. gr. (d)	conc.	normality	boil. point (760 mmHg)
HCl	1.18	ca. 35%	ca. 12N	108.6 °C (20.4%)
H <sub>2</sub> SO <sub>4</sub>	1.84	ca. 97%	ca. 36N	330 °C (98.3%)
HNO <sub>3</sub>	1.38	ca. 60%	ca. 14.5N	120.5 °C (68%)
HClO <sub>4</sub>	1.54	ca. 60%	ca. 9N	203 °C (72%)
HF	1.14	ca. 47%	ca. 27N	120 °C (34%)
H <sub>3</sub> PO <sub>4</sub>	ca. 1.7	ca. 85%	ca. 15N	
CH <sub>3</sub> CO <sub>2</sub> H	1.05	ca. 99.5%	ca. 17N	
NH <sub>4</sub> OH	ca. 0.90	ca. 28%(NH <sub>3</sub> )	ca. 15N	
H <sub>2</sub> O <sub>2</sub>		ca. 30%		

#### 1.2. Expression of concentration for standard solution

The concentration of solution being used as standard for titration is denoted by N (normality), M (molarity) and T (titer).

1) **Normality:** Normality is usually abbreviated to N. The solution of 1N is dissolving 1g equivalent of solute in 1l of solution. A 1g equivalent of compound contains 1g atom of hydrogen (1.0079g) or corresponding amounts of other elements. An advantage of the use of normality is that the solutions of the same normality react with the same volume of each counterpart solution. For instance, 10 ml of N/10 HCl standard solution is equivalent to 10 ml of N/10 NaOH standard solution, so that the mixing of these two solutions make a complete neutral solution.

2) **Molarity:** Molarity is commonly abbreviated to M. The solution of 1M contains 1 molar of compound in 1l of the solution. In the cases such as the acids of one unit of base or alkalis of one unit of acid, molarity is equal to normality. In the cases of the compounds of multi-unit of base or acid, molarity is always larger than normality.

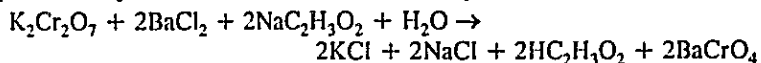
For the complicated example of the relation between molarity and normality, the cases of potassium dichromate solution can be shown as follows. In oxidation-reduction titration, potassium dichromate reacts as an oxidant reagent as;



Thus, unit molecule of potassium dichromate releases three atoms of oxygen which oxidize counter-compound and is equivalent to six atoms of hydrogen. It is

therefore, in this case that 1N solution of potassium dichromate is M/6, which means  $294.18/6 = 49.030\text{g}$  of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 1l.

On the other hand, in precipitation titration, potassium dichromate behaves like the compound of different valence. For example, potassium dichromate can react quantitatively with barium chloride under the presence of sodium acetate as;



Thus, unit molecule of potassium dichromate reacts with two molecules of barium chloride and precipitates two molecules of barium chromate, which are equivalent to four atoms of hydrogen. Therefore, in this case 1N solution of potassium dichromate is M/4, or  $294.18/4 = 73.545\text{g}$  in 1l. So, it should be noticed that the normality of the same potassium dichromate solution is different in the different type of titration. The same examples can be seen for potassium iodate and potassium permanganate.

3) **Titer:** Titer is a value in mg of counter-compound corresponding to 1 ml of standard solution being used for titration. For example, the titer of N/10 potassium dichromate standard solution to ferric oxide is 7.985 mg. The titer of various kinds of standard solution to various counter-components are given in the second chapter of this Appendix.

### 1-3. Preparation of standard solution

Standard solution is classified into three types i.e. for titration, for calibration curve and conductivity measurement. In this Appendix, standard solutions are distinguished from each other according to these types. The amount of reagent mentioned below are of 100% purity, so that for the reagent less than 100% purity the amount should be recalculated to adjust. The use of glass cover, washing the cover and well mixing of the solution after making a constant volume are omitted from the procedures of preparation described below. The prepared solution should be stored in a polyethylene made bottle, if there is no specific bottle mentioned.

#### 1-3-1. Preparation and standardization of the solution for titration

In the following paragraph, f, P and S are designated to factor, preparation procedures and standardization procedures, respectively. Also, the mark + means adding, dissolving and mixing subsequent reagent or water, and  $\rightarrow$  means proceeding to next procedure.

The factor (f) is used as a multiplication factor to normality or molarity. The water used in the following procedures should be the distilled water (or pure water which is distilled after deionizing with resin).

Abbreviations for indicators which are used in standardization are given in Table 4.

#### 1) Standard solution for neutralization titration

N/5 Hydrochloric acid (HCl ca. 17 ml/l)

P: Hydrochloric acid 17 ml + water 1l.

**S:** Sodium carbonate  $\text{Na}_2\text{CO}_3$  (standard reagent) 0.2650g (W g) + water ca. 25 ml + BPB indicator 2~3 drops → titrate by N/5 HCl (to be standardized) → end point (bluish purple → yellow, v ml).

$$f = W/(0.01060*v)$$

**N/10 Hydrochloric acid** (HCl ca. 8.5 ml/l)

**P:** Hydrochloric acid 8.5 ml + water 1l.

**S:** N/10 sodium carbonate standard solution 25.0 ml (V ml) + BPB indicator 2~3 drops → titrate by N/10 HCl (to be standardized) → end point (bluish purple → yellow, v ml).

$$f = V/v$$

**N/20 Hydrochloric acid**

**P:** Dilute precisely the N/10 hydrochloric acid stand. sol. 2 times by water.

**N/6 Nitric acid** ( $\text{HNO}_3$  ca. 11.5 ml/l)

**P:** Nitric acid 11.5 ml + water 1l.

**S:** N/3 sodium hydroxide stand. sol. 10.0 ml (V ml) + water excluded carbon dioxide ca. 50 ml + BPB indicator 2~3 drops → titrate by N/6  $\text{HNO}_3$  (to be standardized) → end point (bluish purple → yellow, v ml).

$$f = V*2/v$$

**N/10 Nitric acid** ( $\text{HNO}_3$  ca. 6.9 ml/l)

**P:** Nitric acid 7 ml + water 1l.

**S:** N/10 sodium hydroxide stand. sol. 25.0 ml (V ml) + BPB indicator 2~3 drops → titrate by N/10  $\text{HNO}_3$  (to be standardized) → end point (bluish purple → yellow, v ml).

$$f = V/v$$

**N/10 Sulfuric acid** ( $\text{H}_2\text{SO}_4$  ca. 2.8 ml/l)

**P:** Water 100 ml + sulfuric acid 3 ml → cool + water 900 ml.

**S:** N/10 sodium carbonate stand. sol. 25.0 ml (V ml) + MR-MB mix-indicator 3~5 drops → titrate by N/10  $\text{H}_2\text{SO}_4$  (to be standardized) → end point (green → grayish purple, pH 4.8, v ml).

$$f = V/v$$

**N/20 Sulfuric acid**

**P:** Dilute precisely the N/10 sulfuric acid stand. sol. 2 times by water.

**N/50 Sulfuric acid**

**P:** Dilute precisely the N/10 sulfuric acid stand. sol. 5 times by water.

**N/3 Sodium hydroxide** ( $\text{NaOH}$  13.33g/l)

**P:** Sodium hydroxide ca. 15g + water 1l + barium hydroxide solution (saturated, prepared fresh) up to no more precipitation → leave 2~3 days without carbon dioxide → decant.

**Preservation:** Store in a polyethylene bottle being attached with a tube filling soda lime.

**S-I:** Weigh precisely sulfamic acid (amidosulfuric acid)  $\text{HSO}_3\text{NH}_2$  (standard reagent) 0.8091g (W g) + water 25 ml + BTB indicator 2~3 drops → titrate by N/3 NaOH (to be standardized) → end point (yellow → blue, v ml).

$$f = W/(0.03236*v)$$

**S-II:** Weigh precisely benzoic acid  $\text{C}_6\text{H}_5\text{CO}_2\text{H}$  (standard reagent) 1.0178g (W g) + ethyl alcohol (95 vol. %) ca. 20 ml + PP indicator a few drops → titrate by N/3 NaOH (to be standardized) → end point (slightly reddish, v ml).

$$f = W/(0.04071*v)$$

**N/5 Sodium hydroxide (NaOH 7.999g/l)**

**P:** Sodium hydroxide ca. 9.5g + water 1l, other procedures are the same as the case of N/3 sodium hydroxide.

**Preservation:** The same as the case of N/3 sodium hydroxide.

**S-I:** Weigh precisely sulfamic acid (standard reagent) 0.4855g (W g) + water 25 ml, other procedures are the same as the case of N/3 sodium hydroxide.

$$f = W/(0.01942*v)$$

**S-II:** Weigh precisely benzoic acid (standard reagent) 0.6110g (W g) + ethyl alcohol (95%) ca. 20 ml, other procedures are the same as the case of N/3 sodium hydroxide.

$$f = W/(0.02443*v)$$

**N/10 Sodium hydroxide (NaOH 4.000g/l)**

**P:** Sodium hydroxide ca. 5g + water 1l, other procedures are the same as the case of N/3 sodium hydroxide.

**Preservation:** The same as the case of N/3 sodium hydroxide.

**S-I:** Weigh precisely sulfamic acid (standard reagent) 0.2428g (W g) + water 25 ml, other procedures are the same as the case of N/3 sodium hydroxide.

$$f = W/(0.00971*v)$$

**S-II:** Weigh precisely benzoic acid (standard reagent) 0.3053g (W g) + ethyl alcohol (95%) ca. 20 ml, other procedures are the same as the case of N/3 sodium hydroxide.

$$f = W/(0.01221*v)$$

**N/20 Sodium hydroxide (NaOH 2.000g/l)**

**P:** Dilute precisely N/10 sodium hydroxide stand. sol. 2 times by water excluded carbon dioxide.

**Preservation:** The same as the case of N/3 sodium hydroxide.

**N/50 Sodium hydroxide**

**P:** Dilute precisely N/10 sodium hydroxide stand. sol. 5 times by water excluded carbon dioxide.

**Preservation:** To be prepared fresh every time.

**N/10 Sodium carbonate ( $\text{Na}_2\text{CO}_3$  5.299g/l)**

**P:** Weigh precisely sodium carbonate  $\text{Na}_2\text{CO}_3$  (standard reagent) 5.299g (W g) + water up to 1000 ml (precise).

$$f = W/5.299$$

**N/20 Sodium carbonate**

**P:** Dilute precisely N/10 sodium carbonate stand. sol. 2 times by water.

**N/10 Barium hydroxide** [ $\text{Ba}(\text{OH})_2$  8.567g/l]

**P:** Barium hydroxide ca. 10g + water 1l → leave 2 days without carbon dioxide → decant.

**Preservation:** Store in a polyethylene bottle being attached with a tube filling soda lime.

**S:** N/10 hydrochloric acid stand. sol. 25.0 ml (V ml) + PP indicator a few drops → titrate by N/10  $\text{Ba}(\text{OH})_2$  (to be standardized) → end point (slightly reddish, v ml).

$$f = V/v$$

## 2) Standard solution for oxidation-reduction titration

**N/5 Potassium permanganate** ( $\text{KMnO}_4$  6.322g/l)

**P:** Potassium permanganate 6.5g + water 1050 ml → Erlenmeyer flask → boil gently for 1~2 hours → leave over night at a dark place → filter using a glass filter (without washing before and after filtration)

**Preservation:** Transfer into a brown bottle which was washed by steam for about 30 minutes and store at a dark place.

**S:** Weigh precisely sodium oxalate  $\text{Na}_2\text{C}_2\text{O}_4$  (standard reagent) 0.3350g (W g) + hot water ca. 200 ml + sulfuric acid (1+1) 10 ml → titrate by N/5  $\text{KMnO}_4$  (to be standardized) → end point (slightly reddish,  $v_1$  ml).

**Blank test:** Hot water ca. 200 ml + sulfuric acid (1+1) 10 ml → titrate by N/5  $\text{KMnO}_4$  (to be standardized) → end point (slightly reddish,  $v_2$  ml).

$$f = W/[0.0134*(v_1 - v_2)]$$

**N/10 Potassium permanganate** ( $\text{KMnO}_4$  3.161g/l)

**P:** Potassium permanganate 3.3g + water 1050 ml, other procedures are the same as the case of N/5 potassium permanganate.

**Preservation:** The same as the case of N/5 potassium permanganate.

**S-I:** Weigh precisely sodium oxalate (standard reagent) 0.2g (W g) + hot water ca. 200 ml, other procedures are the same as the case of N/5 potassium permanganate.

$$f = W/[0.0067*(v_1 - v_2)]$$

**S-II (for antimony determination):** Weigh precisely antimony metal 0.2g (W g) + sulfuric acid 20 ml → dissolve by heating (until disappearing free sulfur) → cool + hydrochloric acid (1+1) 40 ml → Erlenmeyer flask (500 ml) + water up to ca. 200 ml → boil for 2~3 minutes → titrate by N/10  $\text{KMnO}_4$  (to be standardized) → end point (slightly reddish,  $v_1$  ml).

**Blank test:** Sulfuric acid (1+1) 40 ml in a Erlenmeyer flask (500 ml) + hydrochloric acid (1+1) 40 ml + water up to ca. 200 ml → boil for 2~3 minutes

→ titrate by N/5  $\text{KMnO}_4$  (to be standardized) → end point (slightly reddish,  $v_2$  ml).

$$S_b \text{ (mg)} = [W/(v_1 - v_2)] \cdot 1000$$

**N/20 Potassium permanganate** ( $\text{KMnO}_4$  1.581g/l)

**P:** Potassium permanganate 1.7g + water 1050 ml, other procedures are the same as the case of N/5 potassium permanganate.

**Preservation:** The same as the case of N/5 potassium permanganate.

**S:** Weigh precisely sodium oxalate (standard reagent) 0.1g (W g) + hot water ca. 200 ml, other procedures are the same as the case of N/5 potassium permanganate.

$$f = W/[0.00335 \cdot (v_1 - v_2)]$$

**N/40 Potassium permanganate**

**P:** Dilute precisely N/10 potassium permanganate stand. sol. 4 times by water.

**Preservation:** To be prepared fresh each time.

**N/10 Potassium dichromate** ( $\text{K}_2\text{Cr}_2\text{O}_7$  4.904g/l)

**P:** Weigh precisely potassium dichromate (standard reagent) 4.904g (W g) + water up to 1000 ml precise.

**S** (when pure potassium dichromate reagent is not available): N/10 ammonium ferrous sulfate stand. sol. 25.0 ml (V ml) + phosphoric acid 5 ml + water ca. 100 ml + sodium diphenylaminesulfonate indicator 4~5 drops → titrate by N/10  $\text{K}_2\text{Cr}_2\text{O}_7$  (to be standardized) → end point (reddish purple, v ml).

$$f = V/v$$

**N/20 Potassium dichromate**

**P:** Dilute precisely N/10 potassium dichromate 2 times by water.

**N/30 Potassium dichromate**

**P:** Dilute precisely N/10 potassium dichromate 3 times by water.

**N/100 Potassium dichromate**

**P:** Dilute precisely N/20 potassium dichromate 5 times by water.

**N/10 Ammonium ferrous sulfate** [ $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  39.21g/l]

**P:** Ammonium ferrous hexahydrate 40g + sulfuric acid (1+9) 300 ml → cool + water 700 ml

**S-I:** N/10  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$  (to be standardized) 25.0 ml (V ml) + water ca. 25 ml + phosphoric acid ca. 5 ml → titrate by N/10 potassium permanganate stand. sol. → end point (slightly reddish, v ml).

$$f = v/V$$

**S-II:** N/10  $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4$  (to be standardized) 25.0 ml (V ml) + water ca. 25 ml + phosphoric acid ca. 5 ml → titrate by N/10 potassium dichromate stand. sol. → end point (reddish purple, v ml).

$$f = v/V$$

**N/30 Ammonium ferrous sulfate**

**P:** Dilute precisely N/10 ammonium ferrous sulfate stand. sol. 3 times by sulfuric acid (1+32).

**N/10 Ammonium ferric sulfate** [ $\text{FeSO}_4(\text{NH}_4)\text{SO}_4 \cdot 12\text{H}_2\text{O}$  48.22g/l]

**P:** Ammonium ferric sulfate 12-water 48.3g + sulfuric acid (1+29) 300 ml + potassium permanganate sol. (ca. N/10) → slightly reddish + water 700 ml.

**S:** N/10  $\text{FeSO}_4(\text{NH}_4)\text{SO}_4$  (to be standardized) 25.0 ml (V ml) + sulfuric acid (1+1) 15 ml + water ca. 100 ml → reduce with amalgam reduction apparatus\* + phosphoric acid ca. 5 ml → titrate by N/10 potassium permanganate stand. sol. → end point (slightly reddish, v ml).

$$f = v/V$$

**N/10 Sodium thiosulfate** ( $\text{Na}_2\text{S}_2\text{O}_3$  24.82g/l)

**P:** Sodium thiosulfate pentahydrate 26g + anhydrous sodium carbonate 0.2g + water without carbon dioxide 1l + isoamyl alcohol 10 ml → leave 2 days.

**S-I:** Weigh precisely potassium iodate (standard reagent) 0.1g (W g) + water ca. 25 ml → Erlenmeyer flask with cap (100 ml) + potassium iodide 2g + sulfuric acid (1+5) 5 ml → mix well immediately after adding the reagent and then leave it in a dark place for 5 minutes → titrate by N/10 sodium thiosulfate (to be standardized) → slightly yellowish + starch indicator ca. 2 ml → end point (bluish purple → colorless,  $v_1$  ml).

**Blank test:** Erlenmeyer flask with cap (100 ml) + potassium iodide 2g + sulfuric acid (1+5) 5 ml → mix well immediately after adding the reagent and then leave it in a dark place for 5 minutes → titrate by N/10 sodium thiosulfate (to be standardized) → slightly yellowish + starch indicator ca. 2 ml → end point (bluish purple → colorless,  $v_2$  ml).

$$f = W/[0.003567 \cdot (v_1 - v_2)]$$

**S-II (for Cu determination):** Weigh precisely copper metal (standard reagent) 0.2g (W g) + sulfuric acid (1+1) 2 ml + nitric acid (1+1) 10 ml → dissolve by heating → generate white fumes → cool + water ca. 25 ml + ammonium water (1+1) up to smell of ammonium → boil up to non-smell of ammonium → cool + acetic acid 2 ml + water 60 ml + potassium iodide 5g → titrate by N/10 sodium thiosulfate (to be standardized) → slightly yellowish + starch indicator ca. 2 ml → end point (bluish purple → colorless, v ml).

$$\text{Cu (mg)} = (W/v) \cdot 1000$$

**N/20 Sodium thiosulfate**

**P:** Dilute precisely N/10 sodium thiosulfate stand. sol. 2 times by water.

**N/40 Sodium thiosulfate**

**P:** Dilute precisely N/10 sodium thiosulfate stand. sol. 4 times by water.

**N/50 Sodium thiosulfate**

**P:** Dilute precisely N/10 sodium thiosulfate stand. sol. 5 times by water.

---

\* Refer JIS M 8311; Determination of Titanium in Titanium Ores.

#### N/100 Sodium thiosulfate

**P:** Dilute precisely N/10 sodium thiosulfate stand. sol. 10 times by water.

**Preservation:** To be prepared fresh every time.

#### N/10 Iodine (I 12.69g)

**P:** Potassium iodide 40g + water 25 ml + dissolve + water 950 ml.

**Preservation:** Store in a brown bottle and dark place.

**S-I:** N/10 iodine (to be standardized) 25.0 ml (V ml) → titrate by N/10 sodium thiosulfate stand. sol. → slightly yellowish + starch indicator ca. 2 ml → end point (bluish purple → colorless, v ml).

$$f = v/V$$

**S-II (for arsenic determination):** Weigh precisely arsenic trioxide  $As_2O_3$  0.2g (W g) + warm sodium hydroxide sol. (20%) 10 ml → dissolve + PP indicator 1 drop + sulfuric acid (1+10) up to slightly acidic + water 150 ml + sodium hydrogen carbonate 10g → cool + potassium iodide sol. (10%) 3 ml + starch indicator ca. 2 ml → titrate by N/10 iodine (to be standardized) → end point (bluish purple → colorless, v ml).

$$As \text{ (mg)} = [(W \cdot 0.7574)/v] \cdot 1000$$

#### N/20 Iodine

**P:** Dilute precisely N/10 iodine stand. sol. 2 times by water.

#### N/50 Iodine

**P:** Dilute precisely N/10 iodine stand. sol. 5 times by water.

#### N/100 Iodine

**P:** Dilute precisely N/10 iodine stand. sol. 10 times by water.

**Preservation:** To be prepared fresh every time.

#### N/10 Oxalic acid ( $H_2C_2O_4 \cdot 2H_2O$ 6.304g/l)

**P:** Oxalic acid dihydrate 6.3g + water 1l.

**S:** N/10 oxalic acid (to be standardized) 25 ml (V ml) + sulfuric acid (1+1) 20 ml → heat until ca. 70 °C → titrate by N/10 potassium permanganate stand. sol. → end point (slightly reddish, v ml).

$$f = v/V$$

#### N/10 Sodium oxalate ( $Na_2C_2O_4$ 6.700g/l)

**P:** Weigh precisely sodium oxalate (standard reagent) 6.700g (W g) + water up to precisely 1000 ml.

$$f = W/6.7$$

#### N/40 Sodium oxalate

**P:** Dilute precisely N/10 sodium oxalate stand. sol. 4 times by water.

#### N/50 Arsenious acid ( $As_2O_3$ 0.9892g/l)



**P:** Weigh precisely arsenious oxide (arsenious acid, standard reagent) 0.9892g (W g) + warm sodium hydroxide (20%) 15 ml → dissolve + PP indicator 1~2 drops + sulfuric acid (1+1) → (red → colorless) + sodium hydrogen carbonate 1g + water up to precisely 1000 ml.

$$f = W/0.9892$$

**S** (when pure arsenious oxide reagent is not available): N/50 iodine stand. sol. 25.0 ml (V ml) + sodium hydrogen carbonate 2g + water 150 ml → stir for 2~3 min. → titrate by N/50  $\text{As}_2\text{O}_3$  (to be standardized) → light yellow + starch indicator ca. 2 ml → end point (violet → colorless, v ml).

$$f = V/v$$

**N/100 Cerium(IV) sulfate**  $[\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O} \text{ 4.043g/l,}$   
 $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O} \text{ 6.326g/l}]$

**P:** Cerium(IV) sulfate tetrahydrate 4g or  $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  6.5g + sulfuric acid (6+100) 500 ml → filter cloudiness → leave 2 weeks.

**S-I:** Arsenious oxide (Arsenious acid)  $\text{As}_2\text{O}_3$  (standard reagent) 0.2g (W g) + sodium carbonate (5%) 20 ml → dissolve by heating → cool + sulfuric acid (1+5) 25 ml + water up to 100 ml precise → aliquot 5.0 ml + sulfuric acid (1+20) 50 ml +  $\text{OsO}_4$  (0.25%) 3 drops + ferroin indicator (o-phenanthroline monohydrate ferrous complex salt) 1 ml → titrate by N/100 cerium sulfate (to be standardized) → end point (red → colorless ~ light blue,  $v_1$  ml).

**Blank test:** Sulfuric acid (1+20) 50 ml → titrate by N/100 cerium sulfate (to be standardized) → end point (red → colorless ~ light blue,  $v_2$  ml).

$$f = W*5/100/[0.0004946*(v_1 - v_2)]$$

**S-II:** N/10  $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4]$  (standard solution) 2.0 ml (V ml) + water 50 ml + phosphoric acid 5 ml + ferroin indicator 1 ml → titrate by N/100 cerium sulfate (to be standardized) → end point (red → colorless ~ light blue,  $v_1$  ml).

**Blank test:** Water 50 ml + phosphoric acid 5 ml + ferroin indicator 1 ml → titrate by N/100 cerium sulfate (to be standardized) → end point (red → colorless ~ light blue,  $v_2$  ml).

$$f = V*10/(v_1 - v_2)$$

### 3) Standard solution for precipitation titration

**N/10 Silver nitrate** ( $\text{AgNO}_3$  16.99g/l)

**P:** Silver nitrate 17g + water 1000 ml.

**Preservation:** Transfer into a brown bottle which is stored at a dark place.

**S:** N/10 sodium chloride stand. sol. 25.0 ml (V ml) + water 50 ml + potassium chromate indicator 2 ml → titrate by N/10 silver nitrate (to be standardized) → end point (slightly brown, v ml).

$$f = V/v$$

**N/50 Silver nitrate**

**P:** Dilute precisely N/10 silver nitrate stand. sol. 5 times by water.

**N/10 Sodium chloride (NaCl 5.844g/l)**

**P:** Weigh precisely sodium chloride NaCl (standard reagent) 5.844g (W g) + water up to 1000 ml (precise).

$$f = W/5.844$$

**N/10 Ammonium thiocyanate (NH<sub>4</sub>SCN 7.612g/l)**

**P:** Ammonium thiocyanate 8g + water 1000 ml.

**S:** N/10 silver nitrate stand. sol. 25.0 ml (V ml) + water 25 ml + ferric ammonium sulfate indicator 1 ml + nitric acid 2 ml → titrate by N/10 Ammonium thiocyanate (to be standardized) → end point (dark red, v ml).

$$f = V/v$$

**N/20 Ammonium thiocyanate**

**P:** Dilute precisely N/10 ammonium thiocyanate stand. sol. 2 times by water.

#### 4) Standard solution for chelation/complexometric titration

**M/10 Zinc (Zn 6.538g/l)**

**P:** Weigh precisely zinc metal (standard reagent) 6.538g (W g) + water 50 ml + nitric acid 25 ml → dissolve by heating → cool + water up to precisely 1000 ml.

$$f = W/6.538$$

**M/50 Zinc (Zn 1.3076g/l)**

**P:** Weigh precisely zinc metal (standard reagent) 1.3076g (W g) + water 10 ml + nitric acid 5 ml → dissolve by heating → cool + water up to precisely 1000 ml.

$$f = W/1.3076$$

**M/100 Zinc**

**P:** Dilute precisely M/10 zinc stand. sol. 10 times by deionized water.

**M/10 EDTA [Ethylenediamine tetra-acetic acid disodium dihydrate (EDTA) 37.22g/l]**

**P:** EDTA 37.5g + water 1000 ml.

**S:** M/10 zinc stand. sol. 25.0 ml (V ml) + water 100 ml + buffer solution (pH 10, NH<sub>4</sub>Cl 70g + NH<sub>4</sub>OH 570 ml + water up to 1l) 2 ml + BT indicator 3 drops → titrate by M/10 EDTA (to be standardized) → end point (red → perfectly blue, v ml).

$$f = V/v$$

**M/50 EDTA (EDTA 7.445g/l)**

**P:** EDTA 7.5g + water 1000 ml.

**S:** M/50 Zinc stand. sol. 25.0 ml (V ml) + water 100 ml, other procedures are the same as the case of M/10 EDTA (v ml).

$$f = V/v$$

**M/100 EDTA (EDTA 3.722g/l)**

**P:** EDTA 3.8g + water 1000 ml.

S: M/100 Zinc stand. sol. 25.0 ml (V ml) + water 100 ml, other procedures are the same as the case of M/10 EDTA (v ml).

$$f = V/v$$

### 5) Standard solution for other titration

N/100 Thorium nitrate [ $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  5.521g/l]

P: Thorium nitrate 5.5g + water 1000 ml.

S (for fluorine determination): Standard stock sol. of fluoride ion (1.0 mg  $\text{F}^-$ /ml) 5.0 ml (W mg) + water 15 ml + sodium alizarin sulfonate (Alizarin red S) indicator 1.5 ml + sodium hydroxide (0.02%) → violet + hydrochloric acid (1+400) → colorless + buffer sol. (pH 3.5) 3 ml + ethyl alcohol 30 ml → titrate by N/100 thorium nitrate (to be standardized) → end point (the same pink color as blank test,  $v_1$  ml).

Blank test: Water 20 ml + alizarin red S indicator 1.5 ml → subsequent procedures are the same as above + N/100 thorium nitrate (to be standardized) 0.1 ml (precise,  $v_2$  ml) → pink color (referred to the titration above). Correspondent fluorine to 1 ml of the N/100 thorium nitrate can be calculated as follow;

$$F \text{ (g)} = W/1000/(v_1 - v_2)$$

Mercury(II) nitrate [ $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  2.42g/l, 0.5 mg Cl 7ml]

P: Mercury(II) nitrate hydroxide 2.4g + nitric acid (1+80) 20 ml + water up to 1000 ml.

S (for chloride ion determination): Standard stock sol. of chloride ion (1.0 mg  $\text{Cl}^-$ /ml) 50.0 ml (W mg) + water 50 ml + s-diphenylcarbazone mixed indicator 5 drops + nitric acid (1+100) → blue → sea green ~ olive (pH ca. 3.7) → titrate by mercury(II) nitrate (to be standardized) → end point (sea green → gray ~ grayish violet → perfectly violet, v ml). Correspondent chloride ion to 1 ml of the mercury stand. sol. can be calculated as follow;

$$\text{Cl (mg)} = W/v$$

Diphenylthiocarbazone-Carbon tetrachloride (abbreviation to Dithizone 0.1g/300 ml)

P: Dithizone 0.1g + carbon tetrachloride 300 ml → filtrate (No. 5A) → separating funnel (1000 ml) [+ ammonia water (1+100) 400 ml → shake → rest → discard organic phase + carbon tetrachloride 10 ml → shake → rest → discard organic phase + carbon tetrachloride 300 ml + hydrochloric acid (1+10) up to water phase becomes blackish violet → shake → rest → transfer organic phase to another separating funnel (1000 ml) → [ repeat ] → transfer organic phase to another separating funnel (500 ml) + water 100 ml → shake → rest → separate organic phase (Dithizone-Carbon tetrachloride) to be stored.

Preservation: Transfer into a brown bottle (500 ml).

S: Silver nitrate stand. sol. [ $100\mu\text{gAg/ml}$ , prepared by the dilution of stand. stock sol. (1.0 mgAg/ml)] 1.0 ml → separating funnel (30 ml) + water 10 ml + nitric acid (1+2) 2 ml [+ Dithizone stand. sol. 0.20 ml with microburette → shake for 30 second → if organic phase is yellowish brown → discard organic phase] →

[repeat] until end point (organic phase shows green). Total consumption of Dithizone stand. sol. (V ml). Another silver nitrate stand. sol. (100µg/ml) 1.0 ml (W µg) → separating funnel (30 ml) + water 10 ml + nitric acid (1+2) 2 ml + Dithizone stand.sol. (V - 0.2)ml all at once → shake → discard organic phase [+ Dithizone stand. sol. 0.20 ml → shake for 30 sec. → rest → if organic phase is yellowish brown → discard organic phase] → [repeat] until end point (organic phase shows green). Total consumption of Dithizone stand. sol. minus 0.10 ml (v ml). Repeat three times the titration, then calculate average. The correspondent silver (µg) to 1 ml of Dithizone stand. sol. can be calculated as follow;

$$\text{Ag } (\mu\text{g/ml}) = W/v$$

### 1-3-2. Preparation of standard stock solution

Table 2. Procedures for the preparation of standard stock solution (1.0 mg/ml) of common use. ( For 1000 ml stock solution, otherwise mentioned)

Element or oxide	Reagent	Weight (g)	Procedures
Ag	AgNO <sub>3</sub>	1.575	+ HNO <sub>3</sub> (1+9) 100 ml + H <sub>2</sub> O
Al	Al	1.000	+ HCl (1+1) 100 ml → heat → cool + HCl (1+1) 100 ml + H <sub>2</sub> O
Al <sub>2</sub> O <sub>3</sub>	Al	0.5293	+ HCl (1+1) 40 ml → heat → cool + H <sub>2</sub> O
As	As <sub>2</sub> O <sub>3</sub>	1.320	+ NaOH (4%) 20 ml → heat → cool + PP 1 drop + HCl (1+1) → neutral + HCl (1+1) 2 ml + H <sub>2</sub> O
Au	Au	0.100	+ aqua regia 8 ml → heat (water bath) → evaporate to dryness + HCl 1 ml → dryness + HCl (1+1) 20 ml + H <sub>2</sub> O → 100 ml
B <sub>2</sub> O <sub>3</sub>	H <sub>3</sub> BO <sub>3</sub>	1.776	+ hot water ca. 200 ml → cool + H <sub>2</sub> O
Ba	BaCO <sub>3</sub>	1.437	+ H <sub>2</sub> O + HCl (1+1) 100 ml → heat → (CO <sub>2</sub> ↑) → cool + H <sub>2</sub> O
Be - I	Be	0.100	+ HCl (1+1) 20 ml → heat → cool + H <sub>2</sub> O → 100 ml
Be - II (0.1 mg)	BeO	0.1388	+ K <sub>2</sub> S <sub>2</sub> O <sub>7</sub> 2g (porcelain crucible) → fuse → cool + HCl (1+90) → 500 ml
Bi	Bi	1.000	+ HNO <sub>3</sub> (1+1) 30 ml → heat → (NO <sub>2</sub> ↑) → cool + H <sub>2</sub> O
Br <sup>-</sup>	KBr	1.489	+ H <sub>2</sub> O
CN <sup>-</sup>	KCN	1.251	+ H <sub>2</sub> O → 500 ml, standardized by N/10 AgNO <sub>3</sub>

Ammonium Iron(III) Sulfate $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$	brick red	10g + $\text{H}_2\text{SO}_4$ (1+2) 10 ml + $\text{H}_2\text{O}$ 90 ml
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v) Anion titration indicators

Indicator	Discoloration	Procedures
Sodium Alizarin Sulfonate	strong violet → colorless → pink	0.02g + $\text{H}_2\text{O}$ → 100 ml
Diphenylcarbazone- Bromophenol Blue (Diphenylcarbazone mix)	sea green → grayish blue → violet	DC 0.5g + BPB 0.05g + XC-FF 0.12g + ethanol (95%) 100 ml

vi) Chelation/complexometric titration indicators

\* keep in a brown bottle

Indicator	Abbr.	Procedures	Preservation
Eriochrome Black T	BT	0.2g + Triethanolamine 15 ml + ethanol (95%) 5 ml	~ 1 year
2-Hydroxy-1-(2-hydroxy-4-Sulfo-1-Naphthylazo)-3-Naphthoic Acid	NN	1g + $\text{K}_2\text{SO}_4$ 50g → crush + mix in a mortar	stable for a long time
1-(2-Pyridylazo)-2-Naphthol	PAN	0.1g + ethanol(95%) 100 ml	very stable
1-(2-Pyridylazo)-2-Naphthol + Cu-EDTA	Cu- PAN	PAN 0.1g + Cu-EDTA 1.3g + Dioxane(50%) 100 ml	very stable
Cresolphthalein Complexon	PC	0.1g + methanol 100 ml	~ 6 months
Thymolphthalein Complexon	TPC	1g + $\text{KNO}_3$ 100g → crush & mix in a mortar	very stable
Calcein		0.2g + $\text{K}_2\text{SO}_4$ 20g → crush & mix in a mortar	less than 1 year
Xylenol Orange	XO	0.1g + $\text{H}_2\text{O}$ 100 ml	3 ~ 6 months
Methylthymol Blue	MTB	1g + $\text{KNO}_3$ 100g → crush & mix in a mortar	~ 1 year
Protocatechol Violet	PV	0.1g + $\text{H}_2\text{O}$ 100 ml	~ 6 months
Pyrogallol Red	PR	0.05g + ethanol (50%) 100 ml	very stable
Chromazurol S		0.2g + $\text{H}_2\text{O}$ 100 ml	very stable
Salicylic Acid		2g + ethanol (95%) 100 ml	very stable
Sulfosalicylic Acid		2g + $\text{H}_2\text{O}$ 100 ml	very stable
Tiron		2g + $\text{H}_2\text{O}$ 100 ml	very stable
Zircon		0.13g + NaOH (1N) 2 ml + $\text{H}_2\text{O}$ → 100 ml	~ 1 week
Alizarin S		0.1g + $\text{H}_2\text{O}$ 100 ml	~ 6 months
Murexide	MX	0.4g + $\text{K}_2\text{SO}_4$ 100g → crush & mix in a mortar	~ 1 year
Variamine Blue B	VBB	1g + NaCl 100g → crush & mix in a mortar	~ 6 months in a cool & dark place
p-Dimethylaminobenzylidene rhodanine		0.01g + acetone 50 ml	

Methyl Orange - Xylene Cyanol FF - Phenolphthalein	4.2 (lead gray), 8.8 (lead gray), (alkali) pink ↔ violet ↔ lead gray (pH 8.8) ↔ green ↔ grayish green ↔ lead gray (pI 4.2) ↔ claret ↔ vermillion (acid)	MO - XC-FF sol. 10 ml + PP sol. (1%) 6ml
Bromocresol Green - Methyl Red	5.0 (claret) (alkali) green ↔ claret ↔ pink (acid)	BCG 0.3g + MR 0.2g + ethanol (90%) 400ml
Methyl Red - Methylene Blue	5.4 (grayish blue) (alkali) green ↔ grayish blue ↔ claret (acid)	MR 0.1g + MB 0.1g + ethanol (95%) → 200 ml
Bromocresol Green - Chlorophenol Red	6.1 (pale purple) (alkali) ultra- marine ↔ pale purple ↔ blue ↔ sea green ↔ olive (acid)	BCG 0.1g + CPR 0.1g + ethanol (90%) 200ml
Neutral Red - Bromothymol Blue	7.1 (light red) (alkali) blue ↔ grayish green ↔ light red ↔ vermillion (acid)	NR 0.1g + BTB 0.1g + ethanol (90%) 200ml
Bromothymol Blue - Phenol Red	7.4 (light violet) (alkali) violet ↔ light violet ↔ dark green ↔ yellow (acid)	BTB 0.1g + PR 0.1g + ethanol (90%) 50 ml + H <sub>2</sub> O → 200 ml
Cresol Red - Thymol Blue	8.3 (orange red) (alkali) violet ↔ orange red ↔ yellow (acid)	CR 0.1g + TB 0.3g + ethanol (95%) 100 ml + H <sub>2</sub> O → 400 ml
Phenolphthalein - α-Naphtholphthalein	8.9 (light green) (alkali) violet ↔ light green ↔ light red (acid)	PP 0.15g + NP 0.05g + ethanol (95%) 100ml
Thymol blue - Phenolphthalein	9.0 (green) (alkali) violet ↔ green ↔ yellow (acid)	TB 0.1g + PP 0.3g + ethanol (50%) 400 ml
Phenolphthalein - Thymolphthalein	9.9 (red) (alkali) violet ↔ red ↔ colorless (acid)	PP 0.1g + TP 0.1g + ethanol (90%) 200 ml

iii) Indicators for Oxidation - Reduction titration

\* keep in a brown bottle

Indicator	Discolor Reduction → Oxidation (elec. V.)	Procedures
Diphenylamine	colorless → ultra-marine (0.76)	1g + H <sub>2</sub> SO <sub>4</sub> 100 ml *
4-Diphenylamine sulfonic acid sodium	colorless → claret (0.83)	0.25g + H <sub>2</sub> O 100 ml
o-Phenanthroline-Ferrous Sulfate (Ferroin)	red → light blue (1.14)	PT-monohydrate 0.49g + Ferrous sulfate 0.23g + H <sub>2</sub> O 100 ml
Starch	colorless → ultra marine	1g + H <sub>2</sub> O ca. 10ml → mix → pour into hot water 200 ml → boil for 1 min. → cool (make it freshly every time)

iv) Precipitation titration indicators

Indicator	Discoloration	Procedures
Potassium Chromate (K <sub>2</sub> CrO <sub>4</sub> )	light brown	5g + H <sub>2</sub> O 100 ml

Bromocresol Green	BCG	yellow 3.8 ↔ 5.4 blue	0.04g + ethanol (95%) 20 ml + H <sub>2</sub> O (→ 100 ml)
2,5-Dinitrophenol		colorless 4.0 ↔ 5.8 yellow	0.1g + ethanol (95%) 20 ml + H <sub>2</sub> O (→ 100 ml)
Methyl Red	MR	red 4.2 ↔ 6.3 yellow	0.2g + ethanol (95%) 90 ml + H <sub>2</sub> O (→ 100 ml)
p-Nitrophenol	PNP	colorless 5.0 ↔ 7.6 yellow	0.2g + H <sub>2</sub> O (→ 100 ml)
Bromocresol Purple	BCP	yellow 5.2 ↔ 6.8 purple	0.05g + ethanol (95%) 20 ml + H <sub>2</sub> O (→ 100 ml)
Chlorophenol Red	CPR	yellow 5.0 ↔ 6.6 red	0.1g + ethanol (95%) 20 ml + H <sub>2</sub> O (→ 100 ml)
Bromothymol Blue	BTB	yellow 6.0 ↔ 7.6 blue	0.1g + ethanol (95%) 20 ml + H <sub>2</sub> O (→ 100 ml)
Phenol Red	PR	yellow 6.8 ↔ 8.4 red	0.1g + ethanol (95%) 20 ml + H <sub>2</sub> O (→ 100 ml)
Neutral Red		red 6.8 ↔ 8.0 yellow	0.1g + ethanol (95%) 70 ml + H <sub>2</sub> O (→ 100 ml) *
Cresol Red	CR	yellow 7.2 ↔ 8.8 red	0.1g + ethanol (95%) 20 ml + H <sub>2</sub> O (→ 100 ml)
m-Cresol Purple	MCP	yellow 7.4 ↔ 9.0 purple	0.1g + ethanol (95%) (→ 100 ml)
Thymol Blue (alkali)	TB	yellow 8.0 ↔ 9.6 blue	0.1g + ethanol (95%) 20 ml + H <sub>2</sub> O (→ 100 ml)
Phenolphthalein	PP	colorless 8.3 ↔ 10.0 pink	0.1g + ethanol (95%) 90 ml + H <sub>2</sub> O (→ 100 ml)
o-Cresolphthalein	OCP	colorless 8.2 ↔ 9.8 pink	0.1g + ethanol (95%) 90 ml + H <sub>2</sub> O (→ 100 ml)
Thymolphthalein	TP	colorless 9.3 ↔ 10.5 blue	0.1g + ethanol (95%) 90 ml + H <sub>2</sub> O (→ 100 ml)
Alizarin Yellow GG		yellow 10.0 ↔ 12.0 tan	0.1g + H <sub>2</sub> O (→ 100 ml)
Tropaeolin O		yellow 11.0 ↔ 13.0 brown	0.1g + H <sub>2</sub> O (→ 100 ml)
1,3,5-Trinitrobenzene		colorless 11.5 ↔ 14.0 orange	0.1g + ethanol (95%) 70 ml + H <sub>2</sub> O (→ 100 ml)

#### ii) Mixed indicators

Indicator	Discolor range (pH)	Procedures
Methyl Orange - Xylene Cyanol FF	3.8 (lead gray) (alkali) green ↔ grayish green ↔ lead gray ↔ brick (acid)	MO 1g + XC-FF 1.4g + ethanol (50%) 500ml
Methyl Orange - Indigo Carmine	4.1 (lead gray) (alkali) green ↔ lead gray ↔ violet (acid)	MO 0.1g + IC 0.25g + H <sub>2</sub> O → 100 ml
Bromocresol Green - Dimethyl yellow	4.2 (yellow) (alkali) blue ↔ green ↔ yellow ↔ red (acid)	BCG 0.8g + DMY 0.25g + H <sub>2</sub> O → 100ml

U <sub>3</sub> O <sub>8</sub>	U <sub>3</sub> O <sub>8</sub>	1.000	+ HCl 20 ml → heat → cool + H <sub>2</sub> O
V - I	NH <sub>4</sub> VO <sub>3</sub>	2.296	+ hot H <sub>2</sub> O 200 ml → cool + HCl (1+1) 50 ml + H <sub>2</sub> O
V - II	NH <sub>4</sub> VO <sub>3</sub>	2.296	+ hot H <sub>2</sub> O 200 ml → cool + H <sub>2</sub> SO <sub>4</sub> (1+1) 10 ml + H <sub>2</sub> O
W	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	1.794	+ H <sub>2</sub> O
W	WO <sub>3</sub>	1.261	+ hot NaOH (2%) 100 ml → dissolve → cool + H <sub>2</sub> O
WO <sub>3</sub>	Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O	1.423	+ H <sub>2</sub> O
Zn	Zn	1.000	+ HCl (1+1) 20 ml → heat → cool + H <sub>2</sub> O
Zr	Zr	1.000	+ (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> 10g + H <sub>2</sub> SO <sub>4</sub> 25 ml → heat → cool + H <sub>2</sub> SO <sub>4</sub> (1+1) 120 ml → cool + H <sub>2</sub> O

Table 3. Preparation of standard stock solution for sea water

Element or ion (μg at)	Reagent	Weight (g)	Procedures
NH <sub>4</sub> <sup>+</sup> (10)	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.6607	+ H <sub>2</sub> O + chloroform 0.2 ml
NO <sub>2</sub> <sup>-</sup> (10)	NaNO <sub>2</sub>	0.6900	+ H <sub>2</sub> O
NO <sub>3</sub> <sup>-</sup> (10)	KNO <sub>3</sub>	0.1011	+ H <sub>2</sub> O
P (2.0)	KH <sub>2</sub> PO <sub>4</sub>	0.2722	+ H <sub>2</sub> O + chloroform 0.2 ml
Si (5.0)	SiO <sub>2</sub>	0.300	+ Na <sub>2</sub> CO <sub>3</sub> 1g (Pt crucible) → fuse + hot H <sub>2</sub> O + NaOH 5g → dissolve → cool + H <sub>2</sub> O

Table 4. Preparation of indicators for titration

i) Neutralization indicators

\* keep in a brown bottle

Indicator	Abbr.	Discolor range (pH)	Procedures
Metanil Yellow		red 1.2 ↔ 2.3 yellow	0.1g + H <sub>2</sub> O (→ 100 ml)
Thymol Blue (acid)	TB	red 1.2 ↔ 2.8 yellow	0.1g + ethanol (95%) 20 ml + H <sub>2</sub> O (→ 100 ml)
m-Cresol Purple	MCP	red 1.2 ↔ 2.8 yellow	0.1g + NaOH (0.02N) 13.6 ml + H <sub>2</sub> O (→ 250 ml)
Tropaeolin OO		red 1.3 ↔ 3.2 yellow	1.0g + H <sub>2</sub> O (→ 100 ml)
2,6-Dinitrophenol		colorless 2.4 ↔ 4.0 yellow	0.1g + ethanol (95%) 50 ml + H <sub>2</sub> O (→ 100 ml)
Methyl Yellow	MY	red 2.9 ↔ 4.0 yellow	0.1g + ethanol (95%) 90 ml + H <sub>2</sub> O (→ 100 ml)
Bromophenol Blue	BPB	yellow 3.0 ↔ 4.6 violet	0.1g + ethanol (95%) 20 ml + H <sub>2</sub> O (→ 100 ml)
Methyl Orange	MO	red 3.1 ↔ 4.4 orange	0.1g + H <sub>2</sub> O (→ 100 ml)
Congo Red		violet 3.0 ↔ 5.0 red	0.1g + H <sub>2</sub> O (→ 100 ml)



Rh	Rh	0.100	+ $K_2S_2O_7$ 1 ~ 2g(quartz crucible) → fuse → + hot $H_2SO_4$ (1+35) → cool + $H_2SO_4$ (1+35) → 100 ml
Ru	$RuCl_3$	0.2	+ HCl 2 ml + $H_2O$ 20 ml + HCl 15 ml + $H_2O$ → 100 ml, aliquot 10 ml precisely. Standardized by gravimetric method
$SO_4^{2-}$	$K_2SO_4$	1.814	+ $H_2O$
Sb	Sb	0.100	+ aqua regia 30 ml → heat → cool + HCl (1+1) → 100 ml
Se	Se	1.000	+ $HNO_3$ 20 ml → heat → dry up (water bath) → cool + $H_2O$
Se	$SeO_2$	1.405	+ $H_2O$
Si	$SiO_2$	0.214	+ $Na_2CO_3$ 2g (Pt crucible) → fuse → cool + hot $H_2O$ → cool + $H_2O$ → 100 ml
$SiO_2$	$SiO_2$	1.000	+ $Na_2CO_3$ 10g (Pt crucible) → fuse → cool + hot $H_2O$ → cool + $H_2O$
Sn - I	Sn	1.000	+ HCl (1+1) 100 ml → heat → cool + HCl (1+1)
Sn - II	Sn	1.000	+ $H_2SO_4$ (1+5) 50 ml → heat → cool + $H_2SO_4$ (1+5)
Sr	$SrCO_3$	1.685	+ HCl (1+1) 100 ml → heat → ( $CO_2 \uparrow$ ) → cool + $H_2O$
SrO	$SrCO_3$	1.425	+ HCl (1+1) 100 ml → heat → ( $CO_2 \uparrow$ ) → cool + $H_2O$
Ta	$Ta_2O_5$	0.1221	+ $K_2S_2O_7$ 5g(quartz crucible) → fuse → cool + $(NH_4)_2C_2O_4$ (4%) 75 ml + $H_2O$ → 100 ml
Te	Te	1.000	+ HCl 30 ml + $HNO_3$ 10 ml → heat (water bath) → dry up [+ HCl 10 ml → dry up ] → [repeat] 2 times + HCl 80 ml + $H_2O$
Th	$Th(NO_3)_4 \cdot 4H_2O$	1.5	+ $H_2O$ + $HNO_3$ 5 ml + $H_2O$ → 100 ml, aliquot 10 ml precisely → titrate by M/100 EDTA stand., according to result, aliquot (Th 100 mg) precisely + $H_2O$ → 100 ml
Ti	Ti	1.000	+ HCl (1+1) 50 ml → heat → cool + HCl (1+1)
$TiO_2$ - I	$TiO_2$	1.000	+ $K_2S_2O_7$ 10g(quartz or Pt crucible) → fuse → cool + $H_2SO_4$ (1+19) 100 ml → heat (< 50 °C) → cool + $H_2SO_4$ (1+1) 90 ml → cool + $H_2O$
$TiO_2$ - II	$TiO_2$	1.000	+ $K_2S_2O_7$ 10g (quartz or Pt crucible) → fuse → cool + $H_2SO_4$ (1+9) 50 ml → heat (< 50 °C) → cool + $H_2SO_4$ (1+9)

Mn - II	Mn	1.000	+ HNO <sub>3</sub> 20 ml + H <sub>2</sub> SO <sub>4</sub> (1+1) 20 ml → heat (SO <sub>3</sub> ↑) → cool + H <sub>2</sub> O
MnO	Mn	0.7745	+ HNO <sub>3</sub> 10 ml + H <sub>2</sub> SO <sub>4</sub> (1+1) 20 ml → heat (SO <sub>3</sub> ↑ 10 min.) → cool + H <sub>2</sub> O
Mo	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> · 4H <sub>2</sub> O	1.840	+ H <sub>2</sub> O
Mo	Mo	1.000	+ HNO <sub>3</sub> 50 ml → heat (NO <sub>2</sub> ↑) → cool + H <sub>2</sub> O
MoO <sub>3</sub>	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub> · 4H <sub>2</sub> O	1.227	+ H <sub>2</sub> O
NH <sub>3</sub> <sup>+</sup>	NH <sub>4</sub> Cl	2.965	+ H <sub>2</sub> O
NO <sub>2</sub> <sup>-</sup>	NaNO <sub>2</sub>	1.500	+ H <sub>2</sub> O
NO <sub>3</sub> <sup>-</sup>	KNO <sub>3</sub>	1.631	+ H <sub>2</sub> O
Na	NaCl	2.542	+ H <sub>2</sub> O + HCl (1+1) 20 ml + H <sub>2</sub> O
Na <sub>2</sub> O	NaCl	1.886	+ H <sub>2</sub> O + HCl (1+1) 20 ml + H <sub>2</sub> O
Nb	Nb <sub>2</sub> O <sub>5</sub>	0.1431	+ K <sub>2</sub> S <sub>2</sub> O <sub>7</sub> 3g(quartz crucible) → fuse → cool + H <sub>2</sub> SO <sub>4</sub> 15 ml → heat → cool + H <sub>2</sub> SO <sub>4</sub> (1+1) 50ml + H <sub>2</sub> O → 100 ml
Nb	Nb <sub>2</sub> O <sub>5</sub>	0.1431	+ K <sub>2</sub> S <sub>2</sub> O <sub>7</sub> 3g(quartz crucible) → fuse → cool + (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (2.5%) → 100 ml
Ni - I	Ni	1.000	+ HNO <sub>3</sub> (1+1)100 ml → heat (NO <sub>2</sub> ↑) → cool + H <sub>2</sub> O
Ni - II	Ni	1.000	+ HNO <sub>3</sub> (1+1)40 ml → heat + HClO <sub>4</sub> 10 ml → heat (white fumes) → cool + H <sub>2</sub> O
Os	OsO <sub>4</sub>	1.0	+ NaOH (8%) 200 ml + H <sub>2</sub> O → 700 ml. standardized by N/40 stand. Na <sub>2</sub> S <sub>2</sub> O <sub>1</sub>
P	KH <sub>2</sub> PO <sub>4</sub>	4.394	+ H <sub>2</sub> O
PO <sub>4</sub> <sup>3-</sup>	KH <sub>2</sub> PO <sub>4</sub>	1.433	+ H <sub>2</sub> O
P <sub>2</sub> O <sub>5</sub>	KH <sub>2</sub> PO <sub>4</sub>	1.917	+ H <sub>2</sub> O
Pb - I	Pb	1.000	+ HNO <sub>3</sub> (1+2)100 ml → heat (NO <sub>2</sub> ↑) → cool + H <sub>2</sub> O
Pb - II	Pb(NO <sub>3</sub> ) <sub>2</sub>	1.599	+ H <sub>2</sub> O + HNO <sub>3</sub> 1 ml + H <sub>2</sub> O
Pd	Pd	0.100	+ aqua regia 20 ml → heat → dry up → cool [ + HCl (1+1) 10 ml → dry up ] → [repeat] 3 times + HCl 9 ml + H <sub>2</sub> O → 100 ml
Pt	Pt	0.100	+ aqua regia 20 ml → heat → dry up → cool [ + HCl (1+1) 10 ml → dry up ] → [repeat] 3 times + HCl 4 ml + H <sub>2</sub> O → 100 ml
Rb	RbCl	0.1415	+ H <sub>2</sub> O + HCl (1+1) 2 ml + H <sub>2</sub> O → 100 ml

Ca	CaCO <sub>3</sub>	2.497	+ HCl (1+1) 100 ml → heat → (CO <sub>2</sub> ↑) → cool + H <sub>2</sub> O
Cd - I	Cd	1.000	+ HNO <sub>3</sub> (1+1) 20 ml → heat → evaporate to dry (water bath) + HCl 5 ml → dry up → cool + HCl (1+1) 100 ml + H <sub>2</sub> O
Cd - II	CdO	1.142	+ HCl(1+1) 10 ml → heat → cool + H <sub>2</sub> O
Cl <sup>-</sup>	NaCl	1.648	+ H <sub>2</sub> O
Co	Co	1.000	+ HNO <sub>3</sub> 50 ml → heat → (NO <sub>2</sub> ↑) → cool + H <sub>2</sub> O
Cr(III)	Cr	1.000	+ HCl 50 ml → cool + H <sub>2</sub> O
Cr(VI)	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	2.829	+ H <sub>2</sub> O
Cr <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	1.936	+ H <sub>2</sub> O
Cs	CsCl	0.1267	+ H <sub>2</sub> O → 100 ml
Cu - I	Cu	1.000	+ HNO <sub>3</sub> (1+1) 20 ml → heat → (NO <sub>2</sub> ↑) → cool + H <sub>2</sub> O
Cu - II	Cu	1.000	+ HNO <sub>3</sub> (1+2) 20 ml + H <sub>2</sub> SO <sub>4</sub> (1+2) 5 ml → heat → almost dry → cool + H <sub>2</sub> O
F <sup>-</sup>	NaF	2.210	+ H <sub>2</sub> O
Fe	Fe	1.000	+ HCl (1+1) 30 ml → heat → cool + H <sub>2</sub> O
Fe <sub>2</sub> O <sub>3</sub>	Fe	0.6994	+ HNO <sub>3</sub> (1+1) 30 ml → heat + H <sub>2</sub> SO <sub>4</sub> (1+1) 20 ml → heat (white fumes) → cool + H <sub>2</sub> O
Ge	GeO <sub>2</sub>	0.1441	+ Na <sub>2</sub> CO <sub>3</sub> 2g (Pt crucible) → fuse → cool + H <sub>2</sub> O + H <sub>2</sub> SO <sub>4</sub> (1+1) → slightly acidic → heat (CO <sub>2</sub> ↑) → cool + H <sub>2</sub> O → 100 ml
Hg	HgCl <sub>2</sub>	1.353	+ H <sub>2</sub> O + HCl (1+1) 20 ml + H <sub>2</sub> O
I <sup>-</sup>	KI	1.308	+ H <sub>2</sub> O
In	In	0.100	+ HNO <sub>3</sub> 10 ml → heat (NO <sub>2</sub> ↑) → cool + H <sub>2</sub> O → 100 ml
Ir	Ir	0.100	+ Na <sub>2</sub> O <sub>2</sub> 2g (Zr crucible) → fuse → cool + H <sub>2</sub> O + HCl (1+1) → neutral + HCl 5 ml → heat → dry up [+ HCl 5 ml → dry up] → [repeat] 2 times + HCl (1+10) 1 ml + H <sub>2</sub> O 30 ml → filter → filtrate + HCl (1+1) 2 ml + H <sub>2</sub> O → 100 ml
K	KCl	1.907	+ H <sub>2</sub> O + HCl (1+1) 20 ml + H <sub>2</sub> O
K <sub>2</sub> O	KCl	1.583	+ H <sub>2</sub> O + HCl (1+1) 20 ml + H <sub>2</sub> O
Li	LiCl	0.6108	+ HCl (1+1) 2 ml + H <sub>2</sub> O → 100 ml
Li <sub>2</sub> O	LiCl	0.2837	+ H <sub>2</sub> O → 100 ml
Mg	Mg	1.000	+ HCl (1+1) 20 ml → cool + H <sub>2</sub> O
MgO	Mg	0.6031	+ HCl (1+1) 20 ml → cool + H <sub>2</sub> O
Mn - I	Mn	1.000	+ HCl (1+1) 20 ml → heat + H <sub>2</sub> O

## 2. TITER OF STANDARD SOLUTIONS

N/10  $\text{KMnO}_4$  3.1607g/l

1 ml =	5.585mg I <sub>2</sub>	7.185mg FeO	7.985 mg Fe <sub>2</sub> O <sub>3</sub>	2.004mg Ca
	2.804mg CaO	4.790mg Ti	7.990mg TiO <sub>2</sub>	3.198mg Mo
	6.088mg Sb	7.287mg Sb <sub>2</sub> O <sub>3</sub>	1.733mg Cr	2.533mg Cr <sub>2</sub> O <sub>3</sub>
	10.360mg P	11.901mg U	10.449mg Bi	11.649mg Bi <sub>2</sub> O <sub>3</sub>
	3.948mg Se	6.380mg Te	10.218mg Tl	6.700mg Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>
	1.648mg Mn → (Volhard method)			
	1.698mg V & 3.031mg V <sub>2</sub> O <sub>5</sub> → (Zn amalgam - reduction method)			
	5.094mg V & 9.094mg V <sub>2</sub> O <sub>5</sub> → (FeSO <sub>4</sub> - SO <sub>2</sub> -reduction method)			
	14.012mg Ce & 17.212mg CeO <sub>2</sub> → (H <sub>2</sub> O <sub>2</sub> method)			

N/10  $\text{K}_2\text{Cr}_2\text{O}_7$  4.9031 g/l

The titer of this standard solution is the same as those of potassium permanganate. In comparison to potassium permanganate standard, the advantages of this standard are: i) to be able to titrate the components in hydrochloric acid solution, ii) less sensitive to organic compounds, iii) to be able to preserve for long period, and iv) may be used as a basic standard without any further standardization.

N/10  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  27.8011 g/l

N/10  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  39.2130 g/l

1 ml = 1.733mg Cr 2.533mg Cr<sub>2</sub>O<sub>3</sub>

N/10  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  24.8174 g/l

N/10 I 12.690 g/l

1 ml =	0.800mg O	3.545mg Cl	1.733mg Cr	4.903mg $\text{K}_2\text{Cr}_2\text{O}_7$
	1.099mg Mn	6.355mg Cu	6.907mg Pb	3.161mg $\text{KMnO}_4$
	6.088mg Sb	5.934mg Sn		
	7.990mg Br → (KI method)			
	1.069mg S → (BaCrO <sub>4</sub> method)			

N/10 H <sub>2</sub> SO <sub>4</sub>	4.9037 g/l
N/10 HNO <sub>3</sub>	6.3013 g/l
N/10 HCl	3.6461 g/l

1 ml =	3.910mg K	4.710mg K <sub>2</sub> O	5.611mg KOH	10.061mg Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>
	2.299mg Na	3.099mg Na <sub>2</sub> O	4.000mg NaOH	5.004mg CaCO <sub>3</sub>
	4.216mg MgCO <sub>3</sub>			

N/10 NaOH	3.9997 g/l			
1 ml =	0.135mg P	0.309mg P <sub>2</sub> O <sub>5</sub>	9.192mg W	6.183mg H <sub>3</sub> BO <sub>3</sub>

N/10 AgNO <sub>3</sub>	16.9873 g/l (10.7868 g Ag/l)			
1 ml =	2.935mg Ni	3.735mg NiO	3.545mg Cl	14.332mg AgCl
	7.990mg Br	12.690mg I		

### 3. CONVERSION COEFFICIENT TABLE FOR THE WEIGHTS OF CHEMICALS

*A \* A' = B, B \* B' = A, where A and B are the weights equivalent of each chemical*

A	A	B	B'	A'	A	B	B'
	Ag			8.8198	B	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	0.1134
1.3287	Ag	AgCl	0.7526	1.7763	B <sub>2</sub> O <sub>3</sub>	H <sub>3</sub> BO <sub>3</sub>	0.5630
1.5748	Ag	AgNO <sub>3</sub>	0.6350	2.7390	B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O	0.3651
1.0742	Ag	Ag <sub>2</sub> O	0.9310			Ba	
1.1486	Ag	Ag <sub>2</sub> S	0.8706	1.4370	Ba	BaCO <sub>3</sub>	0.6959
0.2474	AgCl	Cl	4.0426	1.5163	Ba	BaCl <sub>2</sub>	0.6595
0.4078	AgCl	NaCl	2.4523	1.8446	Ba	BaCrO <sub>4</sub>	0.5421
0.8437	AgNO <sub>3</sub>	AgCl	1.1853	1.1165	Ba	BaO	0.8957
	Al			1.6995	Ba	BaSO <sub>4</sub>	0.5884
1.8895	Al	Al <sub>2</sub> O <sub>3</sub>	0.5293	0.8455	BaSO <sub>4</sub>	BaCO <sub>3</sub>	1.1827
4.5198	Al	AlPO <sub>4</sub>	0.2213	0.8922	BaSO <sub>4</sub>	BaCl <sub>2</sub>	1.1208
17.5816	Al	KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	0.0569	0.6570	BaSO <sub>4</sub>	BaO	1.5221
	As			0.8220	BaCrO <sub>4</sub>	BaCl <sub>2</sub>	1.2165
1.3203	As	As <sub>2</sub> O <sub>3</sub>	0.7574	0.6053	BaCrO <sub>4</sub>	BaO	1.6522
1.5339	As	As <sub>2</sub> O <sub>5</sub>	0.6520			Be	
1.6419	As	As <sub>2</sub> S <sub>3</sub>	0.6091	7.6527	Be	BeCO <sub>3</sub>	0.1306
2.0698	As	As <sub>2</sub> S <sub>5</sub>	0.4831	2.7753	Be	BeO	0.3603
2.0718	As	Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub>	0.4827	10.6505	Be	Be <sub>3</sub> P <sub>2</sub> O <sub>7</sub>	0.0939
1.1617	As <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> O <sub>5</sub>	0.8608			Bi	
1.2435	As <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> S <sub>3</sub>	0.8042	1.1148	Bi	Bi <sub>2</sub> O <sub>3</sub>	0.8970
1.5676	As <sub>2</sub> O <sub>3</sub>	As <sub>2</sub> S <sub>5</sub>	0.6379	1.2462	Bi	BiOCl	0.8024
1.5692	As <sub>2</sub> O <sub>3</sub>	Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub>	0.6373	1.2301	Bi	Bi <sub>2</sub> S <sub>3</sub>	0.8129
1.3507	As <sub>2</sub> O <sub>5</sub>	Mg <sub>2</sub> As <sub>2</sub> O <sub>7</sub>	0.7404	1.1178	Bi <sub>2</sub> O <sub>3</sub>	BiOCl	0.8946
	Au			1.1034	Bi <sub>2</sub> O <sub>3</sub>	Bi <sub>2</sub> S <sub>3</sub>	0.9063
1.5400	Au	AuCl <sub>3</sub>	0.6494			Br	
2.0910	Au	HAuCl <sub>4</sub> ·4H <sub>2</sub> O	0.4783	2.3500	Br	AgBr	0.4255
	B			1.0126	Br	HBr	0.9875
3.2201	B	B <sub>2</sub> O <sub>3</sub>	0.3106	1.3500	Br	Ag	0.7408
5.7199	B	H <sub>3</sub> BO <sub>3</sub>	0.1748	1.7937	Br	AgCl	0.5575

A	A	B	B'	A'	A	B	B'
0.1001	Br	O	9.9884	3.7347	Cr	K <sub>2</sub> CrO <sub>4</sub>	0.2678
		C		6.2158	Cr	PbCrO <sub>4</sub>	0.1609
3.6641	C	CO <sub>2</sub>	0.2729	2.8289	Cr	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.3535
4.9962	C	CO <sub>1</sub>	0.2002	1.3158	Cr <sub>2</sub> O <sub>3</sub>	CrO <sub>3</sub>	0.7600
16.4299	C	BaCO <sub>3</sub>	0.0609	1.3045	K <sub>2</sub> CrO <sub>4</sub>	BaCrO <sub>4</sub>	0.7666
8.3331	C	CaCO <sub>3</sub>	0.1200			Cs	
4.6690	C	CaO	0.2142	1.2668	Cs	CsCl	0.7894
2.5028	CN	KCN	0.3996	1.0602	Cs	Cs <sub>2</sub> O	0.9132
1.3635	CO <sub>2</sub>	CO <sub>1</sub>	0.7334	2.5342	Cs	Cs <sub>2</sub> PtCl <sub>6</sub>	0.3946
4.4840	CO <sub>2</sub>	BaCO <sub>3</sub>	0.2230	2.0006	CsCl	Cs <sub>2</sub> PtCl <sub>6</sub>	0.4999
2.2743	CO <sub>2</sub>	CaCO <sub>3</sub>	0.4397	2.3903	Cs <sub>2</sub> O	Cs <sub>2</sub> PtCl <sub>6</sub>	0.4184
1.2742	CO <sub>2</sub>	CaO	0.7848			Cu	
		Ca		1.1259	Cu	Cu <sub>2</sub> O	0.8882
2.4972	Ca	CaCO <sub>3</sub>	0.4004	1.2518	Cu	CuO	0.7989
3.1961	Ca	CaC <sub>2</sub> O <sub>4</sub>	0.3129	1.2523	Cu	Cu <sub>2</sub> S	0.7986
1.9480	Ca	CaF <sub>2</sub>	0.5133	3.9291	Cu	CuSO <sub>4</sub> ·5H <sub>2</sub> O	0.2545
1.3992	Ca	CaO	0.7147	1.1118	Cu <sub>2</sub> O	CuO	0.8994
3.3967	Ca	CaSO <sub>4</sub>	0.2944	1.1122	Cu <sub>2</sub> O	Cu <sub>2</sub> S	0.8991
0.4397	CaCO <sub>3</sub>	CO <sub>2</sub>	2.2742	1.0004	CuO	Cu <sub>2</sub> S	0.9996
1.1089	CaCO <sub>3</sub>	CaCl <sub>2</sub>	0.9018	1.2019	CuO	CuS	0.8320
1.3602	CaCO <sub>3</sub>	CaSO <sub>4</sub>	0.7352	3.1388	CuO	CuSO <sub>4</sub> ·5H <sub>2</sub> O	0.3186
0.5603	CaCO <sub>3</sub>	CaO	1.7848	1.2014	Cu <sub>2</sub> S	CuS	0.8323
1.9791	CaO	CaCl <sub>2</sub>	0.5053	3.1376	Cu <sub>2</sub> S	CuSO <sub>4</sub> ·5H <sub>2</sub> O	0.3187
2.4276	CaO	CaSO <sub>4</sub>	0.4119			F	
0.7848	CaO	CO <sub>2</sub>	1.2742	2.0548	F	CaF <sub>2</sub>	0.4867
1.7144	CaSO <sub>4</sub>	BaSO <sub>4</sub>	0.5833	1.0531	F	HF	0.9196
		Cd		1.9513	HF	CaF <sub>2</sub>	0.5125
1.1423	Cd	CdO	0.8754			Fe	
1.2852	Cd	CdS	0.7781	1.2865	Fe	FeO	0.7773
		Ce		1.4297	Fe	Fe <sub>2</sub> O <sub>3</sub>	0.6994
1.1713	Ce	Ce <sub>2</sub> O <sub>3</sub>	0.8538	1.3820	Fe	Fe <sub>2</sub> O <sub>4</sub>	0.7236
1.2284	Ce	CeO <sub>2</sub>	0.8141	1.5741	Fe	FeS	0.6353
1.0487	Ce <sub>2</sub> O <sub>3</sub>	CeO <sub>2</sub>	0.9535	2.1481	Fe	FeS <sub>2</sub>	0.4655
		Cl		4.9781	Fe	FeSO <sub>4</sub> ·7H <sub>2</sub> O	0.2009
4.0426	Cl	AgCl	0.2474	1.1113	FeO	Fe <sub>2</sub> O <sub>3</sub>	0.8998
1.0284	Cl	HCl	0.9724	1.0742	FeO	Fe <sub>2</sub> O <sub>4</sub>	0.9309
2.1028	Cl	KCl	0.4756	0.9660	Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>4</sub>	1.0346
1.6485	Cl	NaCl	0.6066	1.5025	Fe <sub>2</sub> O <sub>3</sub>	FeS <sub>2</sub>	0.6656
3.0426	Cl	Ag	0.3287	8.9723	Fe <sub>2</sub> O <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> Fe(SO <sub>4</sub> ) <sub>2</sub> ·24H <sub>2</sub> O	0.1115
0.6485	Cl	Na	1.5421			Ga	
0.2544	AgCl	HCl	3.9308	1.3442	Ga	Ga <sub>2</sub> O <sub>3</sub>	0.7439
0.5202	AgCl	KCl	1.9224			Ge	
0.4078	AgCl	NaCl	2.4523	1.4408	Ge	GeO <sub>2</sub>	0.6941
		Co				H	
1.2715	Co	CoO	0.7865	36.1751	H	HCl	0.0276
1.3620	Co	Co <sub>2</sub> O <sub>4</sub>	0.7342	8.9370	H	H <sub>2</sub> O	0.1119
1.0712	CoO	Co <sub>3</sub> O <sub>4</sub>	0.9336	48.6524	H	H <sub>2</sub> SO <sub>4</sub>	0.0206
		Cr				Hf	
1.4616	Cr	Cr <sub>2</sub> O <sub>3</sub>	0.6842	1.1793	Hf	HfO <sub>2</sub>	0.8480
1.9231	Cr	CrO <sub>3</sub>	0.5200			Hg	
4.8722	Cr	BaCrO <sub>4</sub>	0.2053	1.1767	Hg	Hg <sub>2</sub> Cl <sub>2</sub>	0.8498

A'	A	B	B'	A'	A	B	B'	
1.3535	Hg	HgCl <sub>2</sub>	0.7388	1.5836	Mn	MnS	0.6315	
1.0399	Hg	Hg <sub>2</sub> O	0.9617	2.2278	MnO	KMnO <sub>4</sub>	0.4489	
1.0798	Hg	HgO	0.9261	1.0752	MnO	Mn <sub>3</sub> O <sub>4</sub>	0.9301	
1.1598	Hg	HgS	0.8622	1.1128	MnO	Mn <sub>2</sub> O <sub>3</sub>	0.8987	
1.0384	Hg <sub>2</sub> O	HgO	0.9631	1.2255	MnO	MnO <sub>2</sub>	0.8160	
1.1151	Hg <sub>2</sub> O	HgS	0.8966	1.2264	MnO	MnS	0.8154	
1.0742	HgO	HgS	0.9310	1.1399	Mn <sub>3</sub> O <sub>4</sub>	MnO <sub>2</sub>	0.8773	
				1.1013	Mn <sub>2</sub> O <sub>3</sub>	MnO <sub>2</sub>	0.9080	
1.8500	I	I	AgI	0.5405		Mo		
1.0079	I	III	III	0.9921	1.5003	Mo	MoO <sub>3</sub>	0.6665
1.1294	I	AgCl	AgCl	0.8855	1.6683	Mo	MoS <sub>2</sub>	0.5994
1.8354	III	AgI	AgI	0.5448	1.8402	Mo	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub>	0.5434
							-4H <sub>2</sub> O	
		In			1.2266	MoO <sub>3</sub>	(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>24</sub>	0.8153
							-4H <sub>2</sub> O	
1.2090	In	In <sub>2</sub> O <sub>3</sub>	In <sub>2</sub> O <sub>3</sub>	0.8271	1.1120	MoO <sub>3</sub>	MoS <sub>2</sub>	0.8993
		K				N		
1.9068	K	KCl	KCl	0.5244	1.2159	N	NH <sub>3</sub>	0.8225
3.5436	K	KClO <sub>4</sub>	KClO <sub>4</sub>	0.2822	3.8190	N	NH <sub>4</sub> Cl	0.2619
1.2046	K	K <sub>2</sub> O	K <sub>2</sub> O	0.8302	4.7168	N	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.2120
6.2152	K	K <sub>2</sub> PtCl <sub>6</sub>	K <sub>2</sub> PtCl <sub>6</sub>	0.1609	3.2845	N	NO <sub>2</sub>	0.3045
0.3184	K <sub>2</sub> CO <sub>3</sub>	CO <sub>2</sub>	CO <sub>2</sub>	3.1403	4.4268	N	NO <sub>3</sub>	0.2259
1.8584	KCl	KClO <sub>4</sub>	KClO <sub>4</sub>	0.5381	4.4982	N	HNO <sub>3</sub>	0.2223
0.6318	KCl	K <sub>2</sub> O	K <sub>2</sub> O	0.5829	3.6408	NH <sub>3</sub>	NO <sub>3</sub>	0.2747
3.2595	KCl	K <sub>2</sub> PtCl <sub>6</sub>	K <sub>2</sub> PtCl <sub>6</sub>	0.3068	1.4997	NO <sub>2</sub>	NaNO <sub>2</sub>	0.6668
1.9224	KCl	AgCl	AgCl	0.5202	1.6306	NO <sub>3</sub>	KNO <sub>3</sub>	0.6133
2.9118	K <sub>2</sub> O	KClO <sub>4</sub>	KClO <sub>4</sub>	0.3399			NH <sub>4</sub>	
1.1622	K <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	0.6816	0.7765	NH <sub>3</sub>	N	1.2878
5.1595	K <sub>2</sub> O	K <sub>2</sub> PtCl <sub>6</sub>	K <sub>2</sub> PtCl <sub>6</sub>	0.1938	2.9654	NH <sub>3</sub>	NH <sub>4</sub> Cl	0.3372
		La			1.9428	NH <sub>4</sub>	NH <sub>4</sub> OH	0.5147
1.1728	La	La <sub>2</sub> O <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	0.8527	3.6626	NH <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.2730
0.6612	LaCl <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	La <sub>2</sub> O <sub>3</sub>	1.5056		Na		
		Li			2.5421	Na	NaCl	0.3934
5.3228	Li	Li <sub>2</sub> CO <sub>3</sub>	Li <sub>2</sub> CO <sub>3</sub>	0.1879	1.3480	Na	Na <sub>2</sub> O	0.7418
6.1078	Li	LiCl	LiCl	0.1637	0.9068	NaCl	Na <sub>2</sub> CO <sub>3</sub>	1.1028
2.1525	Li	Li <sub>2</sub> O	Li <sub>2</sub> O	0.4646	0.5303	NaCl	Na <sub>2</sub> O	1.8859
7.9196	Li	Li <sub>2</sub> SO <sub>4</sub>	Li <sub>2</sub> SO <sub>4</sub>	0.1263	1.1440	Na <sub>2</sub> O	Cl	0.8741
2.8375	Li <sub>2</sub> O	LiCl	LiCl	0.3524			Nb	
3.6792	Li <sub>2</sub> O	Li <sub>2</sub> SO <sub>4</sub>	Li <sub>2</sub> SO <sub>4</sub>	0.2718	1.4305	Nb	Nb <sub>2</sub> O <sub>5</sub>	0.6990
		Mg				Ni		
3.4690	Mg	MgCO <sub>3</sub>	MgCO <sub>3</sub>	0.2883	1.2726	Ni	NiO	0.7858
1.6583	Mg	MgO	MgO	0.6030		Os		
4.5783	Mg	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	0.2184	1.3365	Os	OsO <sub>4</sub>	0.7482
1.0919	MgO	CO <sub>2</sub>	CO <sub>2</sub>	0.9158		P		
2.0919	MgO	MgCO <sub>3</sub>	MgCO <sub>3</sub>	0.4781	2.2914	P	P <sub>2</sub> O <sub>5</sub>	0.4364
2.7609	MgO	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	0.3622	3.0662	P	PO <sub>4</sub>	0.3261
0.5220	MgCO <sub>3</sub>	CO <sub>2</sub>	CO <sub>2</sub>	1.9158	3.5926	P	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	0.2783
		Mn			1.9174	P <sub>2</sub> O <sub>5</sub>	KH <sub>2</sub> PO <sub>4</sub>	0.5215
1.2912	Mn	MnO	MnO	0.7745	1.5679	P <sub>2</sub> O <sub>5</sub>	Mg <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	0.6378
1.3883	Mn	Mn <sub>2</sub> O <sub>4</sub>	Mn <sub>2</sub> O <sub>4</sub>	0.7203	1.0001	P <sub>2</sub> O <sub>5</sub>	NaH <sub>2</sub> PO <sub>4</sub>	0.9999
1.4368	Mn	Mn <sub>2</sub> O <sub>3</sub>	Mn <sub>2</sub> O <sub>3</sub>	0.6960			Pb	
1.5825	Mn	MnO <sub>2</sub>	MnO <sub>2</sub>	0.6319	1.5598	Pb	PhCrO <sub>3</sub>	0.6411

A'	A	B	B'	A'	A	B	B'
1.0772	Pb	PbO	0.9283			Sn	
1.1544	Pb	PbO <sub>2</sub>	0.8662	1.1348	Sn	SnO	0.8812
1.1547	Pb	PbS	0.8660	1.2696	Sn	SnO <sub>2</sub>	0.7877
1.4636	Pb	PbSO <sub>4</sub>	0.6833	1.5402	Sn	SnS <sub>2</sub>	0.6493
1.4480	PbO	PbCrO <sub>4</sub>	0.6906	0.8938	SnO <sub>2</sub>	SnO	1.1188
1.0717	PbO	PbO <sub>2</sub>	0.9331			Sr	
1.0720	PbO	PbS	0.9329	1.6849	Sr	SrCO <sub>3</sub>	0.5935
1.3587	PbO	PbSO <sub>4</sub>	0.7360	1.1826	Sr	SrO	0.8456
1.3512	PbO <sub>2</sub>	PbCrO <sub>4</sub>	0.7401	2.0963	Sr	SrSO <sub>4</sub>	0.4770
1.2678	PbO <sub>2</sub>	PbSO <sub>4</sub>	0.7888	1.4247	SrO	SrCO <sub>3</sub>	0.7019
1.3508	PbS	PbCrO <sub>4</sub>	0.7403	1.7726	SrO	SrSO <sub>4</sub>	0.5641
1.2675	PbS	PbSO <sub>4</sub>	0.7890			Ta	
		Pt		1.2211	Ta	Ta <sub>2</sub> O <sub>5</sub>	0.8190
2.6548	Pt	H <sub>2</sub> PtCl <sub>6</sub> ·6H <sub>2</sub> O	0.3767			Te	
		Rh		1.2508	Te	TeO <sub>2</sub>	0.7995
1.4148	Rh	RhCl	0.7068			Th	
3.3857	Rh	Rh <sub>2</sub> PtCl <sub>6</sub>	0.2954	1.1379	Th	ThO <sub>2</sub>	0.8788
2.3931	RbCl	Rh <sub>2</sub> PtCl <sub>6</sub>	0.4179			Ti	
1.2937	Rb <sub>2</sub> O	RbCl	0.7730	1.6680	Ti	TiO <sub>2</sub>	0.5995
3.0960	Rb <sub>2</sub> O	Rh <sub>2</sub> PtCl <sub>6</sub>	0.3230			Tl	
		S		1.1735	Tl	TlCl	0.8522
1.9981	S	SO <sub>2</sub>	0.5005	1.0391	Tl	Tl <sub>2</sub> O	0.9623
2.4971	S	SO <sub>3</sub>	0.4005	1.1174	Tl	Tl <sub>2</sub> O <sub>3</sub>	0.8949
2.9962	S	SO <sub>4</sub>	0.3338			U	
7.2797	S	BaSO <sub>4</sub>	0.1374	1.1344	U	UO <sub>2</sub>	0.8815
1.0629	S	H <sub>2</sub> S	0.9408	1.2017	U	UO <sub>3</sub>	0.8322
1.2498	SO <sub>2</sub>	SO <sub>3</sub>	0.8002	1.1792	U	U <sub>3</sub> O <sub>8</sub>	0.8480
1.4995	SO <sub>2</sub>	SO <sub>4</sub>	0.6669	1.0395	UO <sub>2</sub>	U <sub>3</sub> O <sub>8</sub>	0.9620
3.6433	SO <sub>2</sub>	BaSO <sub>4</sub>	0.2745	0.9814	UO <sub>3</sub>	U <sub>3</sub> O <sub>8</sub>	1.0190
2.9152	SO <sub>3</sub>	BaSO <sub>4</sub>	0.3430			V	
2.4297	SO <sub>4</sub>	BaSO <sub>4</sub>	0.4116	1.6282	V	VO <sub>2</sub>	0.6142
2.3797	H <sub>2</sub> SO <sub>4</sub>	BaSO <sub>4</sub>	0.4202	1.7852	V	V <sub>2</sub> O <sub>5</sub>	0.5602
		Sb				W	
1.1971	Sb	Sb <sub>2</sub> O <sub>3</sub>	0.8353	1.2611	W	WO <sub>3</sub>	0.7930
1.3285	Sb	Sb <sub>2</sub> O <sub>5</sub>	0.7527			Y	
1.3950	Sb	Sb <sub>2</sub> S <sub>3</sub>	0.7169	1.2699	Y	Y <sub>2</sub> O <sub>3</sub>	0.7874
1.6583	Sb	Sb <sub>2</sub> S <sub>5</sub>	0.6030			Zn	
1.1098	Sb <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> O <sub>5</sub>	0.9011	1.9179	Zn	ZnCO <sub>3</sub>	0.5214
1.1653	Sb <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> S <sub>3</sub>	0.8582	1.2447	Zn	ZnO	0.8034
1.3853	Sb <sub>2</sub> O <sub>3</sub>	Sb <sub>2</sub> S <sub>5</sub>	0.7219	1.4904	Zn	ZnS	0.6710
1.0500	Sb <sub>2</sub> O <sub>5</sub>	Sb <sub>2</sub> S <sub>3</sub>	0.9524	4.3986	Zn	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	0.2274
1.2482	Sb <sub>2</sub> O <sub>5</sub>	Sb <sub>2</sub> S <sub>5</sub>	0.8011	1.5408	ZnO	ZnCO <sub>3</sub>	0.6490
		Se		1.1974	ZnO	ZnS	0.8352
1.4053	Se	SeO <sub>2</sub>	0.7116			Zr	
		Si		1.3508	Zr	ZrO <sub>2</sub>	0.7403
2.1393	Si	SiO <sub>2</sub>	0.4674				



## APPENDIX II

### 4. A LIST OF INSTRUMENTS FOR CHEMICAL ANALYSIS IN THE GEOSCIENCE LABORATORY

(Symbols , ♦ Type, ▫ Maker and Model, • Attachment)

1. X-Ray Fluorescence Spectrometer (XRF)
  - ♦ Wavelength dispersion and sequential-type
  - RIGAKU ; System 3370
  - Bead sampler (Fusion machine)
  - Manual oil pressure briquetting press
2. Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES)
  - ♦ Multi-elements sequential-type
  - SEIKO INSTRUMENTS , SPS-1500VR
3. Atomic Absorption Spectrophotometer (AAS)
  - ♦ Polarized Zeeman-type
  - HITACHI ; Z-S100
  - Graphite atomizer and auto-sampler
  - Hydride formation system
4. Ultra-Violet Spectrophotometer (UVS)
  - ♦ Double Beam-type
  - HITACHI ; U-2000
5. Mercury Analyzer
  - NIPPON INSTRUMENTS ; MERCURY / SP-3D
6. Fluorine Analyzer
  - LINDBERG / BLUE M , New Minimate Laboratory Tube Furnace
  - VITRO KAGAKU ; Quartz Tube
7. Karl Fischer Moisture Titrator
  - KYOTO ELECTRONICS , MKA-210
  - Evaporative Ore Titration Adaptor (Furnace)
8. Automatic Titrator
  - HIRANUMA ; COM-101
9. Conductivity Meter
  - TOA ELECTRONICS ; CM-60S
10. Ion Analyzer









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