

RAPID SIMULTANEOUS 17 ELEMENTS ANALYSIS OF SOME YAMATO METEORITES BY ICP-OES

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Abstract: Seventeen elements in stone meteorites were determined rapidly and simultaneously by ICP-OES (Inductively Coupled Plasma—Optical Emission Spectroscopy). Five antarctic meteorites were classified by using ICP-OES data. The result is as follows: Yamato-74001 and -75028 are H chondrite and Yamato-74035, -74191 and Allan Hills-769 are L chondrite.

I. Introduction

Elemental abundances in meteorites are very important not only for their classification but also for discussion on their origin and history. Usually, major and some minor elemental abundances are determined by classical wet chemical method (JAROSEWICH, 1966), which is a superior technique because of high precision, but it lacks the rapidity of analysis. Before making various kinds of researches on meteorites, we often wish to know preliminary data on the abundances of elements. So, it is essential to develop a rapid analytical method of meteorites. This paper deals with the application of ICP-OES (Inductively Coupled Plasma—Optical Emission Spectroscopy) to meteorite researches in view of rapid elemental analysis.

The basis of ICP-OES is literally optical emission spectroscopy equipped with inductively coupled plasma as an emission source. Once sample solution is nebulized to aerosol and introduced into ICP, the solution is dehydrated and the component elements are excited because of high temperature in ICP followed by emission of atomic or ionic line lights of these elements. This apparatus was firstly developed by Iowa State University group (FASSEL and KNISELEY, 1974) and commercial machines were popularized after the latter period of the 1970's because they have more improved features than other similar kinds of equipments currently used. They are efficient to analyze many elements simultaneously, to use less than 1 ml of liquid sample for usual analysis, to have wider dynamic analytical range and linearity over 3 to 5 order of magnitudes, to be comparatively free from interelemental interferences, etc. Because of these characteristics, a large number of application studies of ICP-OES methods to many varieties of materials including geochemical materials have been conducted (see review paper by NOTSU, 1980). ONUMA *et al.* (1979) applied this method to the Anlung (Chinese) stone meteorite

and found that it belonged to H chondrite.

2. Experimental

The stone meteorite sample was crushed in an agate mortar and fragments of fusion crusts were removed by hand-picking under a binocular microscope. 300 mg of sample fragments were pulverized under acetone in an agate mortar, dissolved in HF-HClO₄ mixture hot solution on a platinum dish, evaporated to dryness, taken up by 1 ml of HClO₄, then diluted to 100 ml. As stone meteorites are very inhomogeneous, we must take account of the minimum amount of sampling in order to get their bulk chemical compositions. We found that 300 mg is the minimum weight from the viewpoint of sample inhomogeneity. This problem will be discussed in the later section.

The sample solution thus prepared was analyzed by ICP-OES, a Jarrell-Ash PLASMA-ATOMCOMP MODEL 975. The operating conditions of ICP-OES for the present study are summarized in Table 1. In this meteorite analysis, usually 17 elements in sample solution were determined simultaneously. The wave length and detection limit (recalculated to the limit concentration in the meteorite from the 2 σ value of 10 background analysis, when 300 mg of sample is dissolved to 100 ml of solution) for each element, are shown in Table 2. It is important to evaluate the reproducibility of each analyzed value for the same sample solution. Generally, in ICP-OES determination, R.S.D. (relative standard deviation) of 10 ppm solution is between 1 and 2% for almost all elements. The less the concentration in the sample solution, the worse R.S.D.

Although the ICP-OES analysis has a very small interelemental effect, we must reduce this effect for a better determination of samples with complex matrices, such as geochemical or biological materials, which contain major elements of % order and trace elements of less than ppm or ppb order. These effects include other emission line or molecular band interference to the objective emission line, background intensity increase mainly due to stray light, enhancement or decrease of the objective

Table 1. Operating conditions of ICP-OES.

Incident power	1200 W
Reflected power	<10 W
Nebulizer type	Cross flow
Argon flow rate	
Coolant gas	17 l/min
Sample gas	0.5 l/min
Plasma gas	0.6 l/min
Sample aspiration rate	1.0 ml/min
Observation height	11 mm above coil

Table 2. Wave length and detection limit.

Element	Wave length (nm)	Detection limit in meteorite (ppm)**	
Al	309.2	20	as Al ₂ O ₃
Ba	455.4	0.3	
Ca	317.9	10	as CaO
Co	228.6	1.0	
Fe	259.9	2	
Li	670.7	0.3	
Mg	279.5	1.0	as MgO
Mn	257.6	0.5	as MnO
Na	589.0	10	as Na ₂ O
Ni	231.6×2*	5	
P	214.9×2*	100	as P ₂ O ₅
Sc	361.3	0.2	
Sr	407.7	0.3	
Ti	334.9	1.0	as TiO ₂
V	292.4	1.0	
Y	371.0	0.2	
Zn	213.8×2*	1.0	

* 2nd order.

** Recalculated to the limit concentration in the meteorite from the 2 σ value of 10 background intensity measurements, when 300 mg of sample is dissolved to 100 ml of solution.

line intensity with the presence of other elements, etc. In the case of trace element analysis, these effects are sometimes not negligible. HIRANO and ONUMA (in preparation, 1980) have pointed out that these effects were apparently negligible for rock analysis, using the analytical calibration lines which were formed from the USGS standard rock solutions (AGV-1, BCR-1, G-2 and GSP-1), instead of pure solutions without any matrix component. We have adopted this standard rock calibration method in the meteorite analysis. Furthermore, in this meteorite analysis, for some elemental pairs, interelemental corrections due to background increase or line interference were performed using the following empirical correction factors:

Co	(228.6 nm)	from	Fe	$8.3 \times 10^{-5} \%Co/\%Fe$
			Mg	$1.7 \times 10^{-5} \%Co/\%Mg$
			Ni	$1.2 \times 10^{-3} \%Co/\%Ni$
P	(214.9×2 nm)	from	Fe	$1.2 \times 10^{-3} \%P/\%Fe$
			Mg	$3.4 \times 10^{-3} \%P/\%Mg$
V	(292.4 nm)	from	Fe	$2.2 \times 10^{-4} \%V/\%Fe$
			Mg	$1.1 \times 10^{-4} \%V/\%Mg$
Zn	(213.8×2 nm)	from	Fe	$8.6 \times 10^{-5} \%Zn/\%Fe$

Mg	3.1×10^{-4}	%Zn/%Mg
Ni	3.5×10^{-3}	%Zn/%Ni.

3. Results and Discussion

Table 3 shows the analytical results of 5 antarctic chondrites (Yamato-74001, -74035, -74191, -75028 and Allan Hills-769) together with those of the Allende (C3V) and Anlung (H5) chondrites. To compare the data by ICP-OES with those previously reported using other analytical methods, Table 3 also shows the reference data of the same meteorites, as far as available. Accuracy of these data in Table 3 is estimated at 5% or less for elements with contents above 0.1% in the meteorite, 10% or less for 10 to 1000 ppm contents of elements, and much larger for elements below 10 ppm.

The data on the Allende meteorite in this work excellently agree with those by other methods except Zn. However, WOLF *et al.* (1980) reported the Zn content in bulk Allende to be 134 ppm by radiochemical neutron activation analysis. In the case of the Anlung chondrite (ONUMA *et al.*, 1979), total iron (ΣFe), Ni, Co and MgO values for two portions (100 mg each) are different from each other. This indicates a heterogeneous distribution of metallic Fe (and FeS) in the meteorite specimen. Depletion of Fe, Ni and Co in the portion (1) in Table 3 is compensated by enrichment of MgO in the same portion. Averaged values of the two 100 mg portions agree with those by conventional wet chemical analysis (METEORITE LABORATORY, 1974), suggesting that 100 mg of meteoritic sample is too small to obtain bulk chemical composition.

Among 5 antarctic meteorites analyzed by ICP-OES, two (Yamato-74191 and -75028) have been previously determined by conventional wet chemical method by H. HARAMURA (YANAI, 1979). Agreement of two sets of data for each of the two meteorites was good within the accuracy of data, but there existed some exceptions, such as TiO_2 and Co. It is also pointed out that there existed slight differences in ΣFe , MgO and Na_2O between the two sets of data. These kinds of discrepancy may result from the heterogeneity of meteoritic samples. At present, however, we will not make such a conclusion before we reexamine our improved ICP-OES analytical method. There remain many unsolved problems about the application of the ICP-OES method to the analysis of rocks or meteorites.

Despite some exceptional discrepancies between ICP-OES data and other analytical data, ICP-OES analysis of meteorites has many advantages. The merit is that it can determine 17 elements, including some trace elements, simultaneously and rapidly. Although accuracy of major elements determination by ICP-OES is poorer than that of conventional wet chemical analysis, we are able to classify meteorite samples by using ICP-OES data only; *i.e.*, Yamato-74001 and -75028 belong to H chondrite and Yamato-74035, -74191 and Allan Hills-769 to L chondrite.

Table 3. Analytical results.

Name	Yamato-				Allan Hills-769	Anlung			Allende		
	75028	74001	74191	74035		L6 This work	H5		C3V (d) This work	(e)	
Class**	H3 This work	H5 This work	L3 This work	L6 This work	(1)*		(2)* ave.	(c)			
SiO ₂ (%)	—	36.62	40.09	—	—	—	—	35.55	—	34.23	34.28
TiO ₂	0.10	0.16	0.10	0.10	0.10	0.13	0.11	0.12	0.13	0.15	0.15
Al ₂ O ₃	2.2	2.14	2.89	2.2	2.3	2.4	2.2	2.3	3.1	3.27	3.29
ΣFe	24.9	26.29	20.22	21.5	22.4	22.4	30.5	26.5	24.1	23.85	21.11
MnO	0.31	0.30	0.35	0.35	0.34	0.32	0.28	0.30	0.19	0.18	—
MgO	22.2	23.92	24.89	23.7	23.2	24.7	22.6	23.7	23.4	24.62	24.63
CaO	1.52	1.72	1.79	1.69	1.73	1.66	1.41	1.54	2.1	2.61	2.59
Na ₂ O	0.98	0.85	0.97	0.94	1.07	0.85	0.76	0.81	0.51	0.45	0.46
K ₂ O	—	0.10	0.13	—	—	0.09	0.08	0.09	—	0.03	0.03
P ₂ O ₅	0.23	0.37	0.20	0.19	0.17	0.33	0.36	0.35	0.20	0.23	—
ΣNi	1.66	1.54	0.85	1.23	1.51	1.41	1.73	1.57	—	1.39	—
Co (ppm)	640	340	320	560	640	700	1200	950	600	600	—
Zn	33	—	—	24	34	55	59	57	83	25	—
V	83	—	—	81	87	66	73	70	110	70	—
Sr	10	—	—	11	10	11	9.4	10	15	13	12
Sc	9	—	—	9	10	—	—	—	11	11	—
Ba	6	—	—	6	6	2.3	2.2	2.3	7	5	4.1
Y	3	—	—	3	3	—	—	—	3	2	3.1
Li	1.2	—	—	1.9	1.5	1.9	1.8	1.9	1.4	—	—

* ICP-OES analysis using 100 mg sample.

** After YANAI (1979) for antactic meteorites.

(a) YANAI (1979), (b) ONUMA *et al.* (1979), (c) METEORITE LABORATORY (1974), (d) CLARKE *et al.* (1970), (e) MARTIN and MASON (1974).

It is very troublesome to add the chemical separation to analysis of trace elements, like Zn, V, Sr, etc. throughout the conventional wet chemical analysis procedure.

Our improved ICP-OES analysis of meteorites has some demerits. It is the most serious point that silicon cannot be determined because meteorite sample is dissolved in HF-HClO₄ solution in open system and Si escapes as SiF₄ gas. When other chemical decomposition procedure, such as LiBO₂ fusion, is adopted, silicon and some other elements can be determined, but another demerit will arise in this method. The other shortcoming point is that a chemical form of iron cannot be determined separately. In meteorites, iron appears as metallic Fe, troilite (FeS) and Fe in silicate (Fe^{II} and Fe^{III}). Nickel also is in the same situation.

4. Conclusion

Rapid analysis of 17 elements in stone meteorites was carried out by the ICP-OES method. The accuracy of ICP-OES data is poorer than that of conventional wet chemical analysis for major elements; however, such demerits are compensated by simplicity and rapidity. Furthermore, by the ICP-OES method some trace elements can be determined simultaneously with major elements.

The ICP-OES method has been applied to five antarctic meteorites. The results are as follows; Yamato-74001 and -75028 are H chondrite and Yamato-74035, -74191 and Allan Hills-769 are L chondrite.

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