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ELEMENTAL ANALYSIS OF ZEOLITES BY INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPY VIA DIRECT INJECTION

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A method is described for determining the elemental analyses of zeolites in which the elements are determined as ratios of the aluminum content. This method is accurate, significantly faster and allows more rapid repeat analyses (enabling statistical significance of data to be defined) than any other technique currently available. The zeolite in a suspension of xylene is injected directly into the ICPES argon plasma and the metal ratios are measured simultaneously. This technique allows a sample turnaround time of ≈ 15 min with a repeat analysis every 2 min.

Elemental analyses and X-ray diffraction are the traditional methods of defining zeolites. Since zeolites are becoming increasingly important in the petrochemical industry the volume of routine elemental analyses has increased. The analyses of synthetic and natural zeolites, commonly involves digestion steps which include, e.g. fusion with sodium carbonate 1,2) or lithium tetraborate, 2) dissolution in hydrofluoric acid, 1) etc. The sample thus solubilized can then be analyzed by a variety of means including titrimetric, gravimetric 1) and spectroscopic. 2) Analyses of this type are prone to errors both from the number of steps involved in solubilizing the silica, and the type of operation being performed (e.g. fusion can lead to evaporative loss of volatile alkali metals) and are manpower intensive (> 3 h/sample). A device which enables direct powder introduction to ICPES, thus eliminating the fusion step, has recently been reported. 3) Further, a technique for direct injection of powders in a gelatinous slurry has also been reported. 4)

We have found that zeolites can be analyzed by directly injecting a suspension of the zeolite, in a "carrier" fluid such as xylene, into the high temperature argon plasma (>8000 °C) of an ICPES. All of the elements in the ICPES array can thus be simultaneously measured and related as a ratio to a "reference" element within the zeolite. Since it is common practice to define the chemical composition of zeolites as ratios of the elements with respect to aluminum, 5) this procedure is ideally suited to the analysis of zeolites.

This paper compares the elemental analyses of a number of zeolites as measured by this direct injection technique (ICPES (Direct)) with those determined via more conventional techniques, i.e. AAS/fusion, wet chemical, etc.

Finely ground zeolite (≈ 0.1 g) 6) is ultrasonically dispersed in xylene (25 ml). This fluid is then aspirated into the ICPES via a conventional high solids nebulizer 7) and a peristaltic pump. The various elements in the zeolite are measured directly and the instrument calibrated with Conostan Metallo-Organic Standards.[8)] A Jarrell-Ash Atom Comp Plasma Emission Spectrometer was used in this study. The instrument parameters were: RF power 1.5 kW, torch height 13 mm, exposure time 7 s, and aspiration rate 1.5 ml/min. The wavelengths used to monitor the various elements in the study, together with the background corrections are shown in Table 1.

Table 1. Spectrometer Parameters

Element	Wavelength of analyte line/nm	Background
Si	288.1	high wavelength side
Al	308.2	"
K	766.5	(high + low wavelength sides) ÷ 2
Na	589.0	"

Figure 1 shows a comparison of the SiO_2/Al_2O_3 ratio of a number of zeolites (including offretite, omega (mazzite), faujasite, etc.) measured using the current technique (ICPES (Direct)) with those determined by more conventional methods. Good agreement exists between the various techniques used. This figure further shows the estimated error (± 0.5) for a single SiO_2/Al_2O_3 ratio as measured by both ICPES and AAS/fusion techniques. A good estimate of errors in

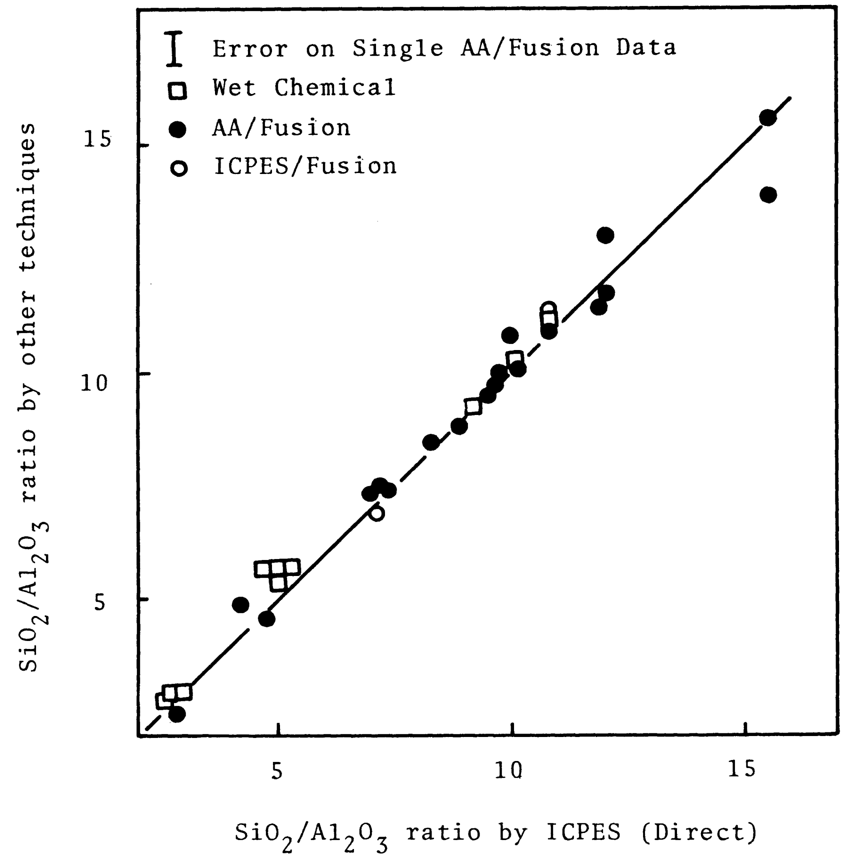

Fig. 1. Comparison of silica/alumina ratio of zeolites as measured by ICPES (Direct) and other techniques.

Table 2. Comparison of Elemental Analyses of Various Zeolites Measured via ICPES (Direct) and Various Other Techniques

Sample No.	AA/Fusion (exceptions noted)			ICPES (Direct)c)		
	SiO_2/Al_2O_3	K_2O/Al_2O_3	Na_2O/Al_2O_3	SiO_2/Al_2O_3	K_2O/Al_2O_3	Na_2O/Al_2O_3
A	9.90	0.92	--	9.75	0.94	--
	(H-offretite fully potassium exchanged)					
B	9.5	0.70	--	9.50	0.70	--
	(TMA-offretite fully potassium exchanged)					
C	9.70	0.25	--	9.78	0.30	--
	(H-offretite fully ammonium exchanged)					
D	7.16	0.83	--	7.16	0.86	--
	7.05 a)	0.88	--			
	6.9 b)	0.85	--			
E	10.9	0.24	--	10.8	0.20	--
	11.43 a)	0.24	--			
	11.2 b)	0.24	--			
F	10.6	0.60	--	10.1	0.52	--
	10.3 b)	0.54	--			
G	15.6	1.1	--	15.5	0.98	--
	13.8	0.99				
H	13.1	0.99	--	12.0	1.04	--
	11.7	0.96				
I	7.38	0.22	--	7.38	0.34	--
J	8.45	--	0.80	8.3	--	0.70
K	7.38	--	0.22	7.01	--	0.18
L	10.8	--	1.06	10.03	--	0.88
M	15.6	--	--	14.7	--	--
N	5.66 b)	--	0.75	5.18	--	0.66
O	5.47 b)	--	0.59	5.02	--	0.56
P	2.95 b)	--	0.85	2.89	--	0.78
Q	2.82 b)	--	0.57	2.56	--	0.55

a) ICPES/fusion.

b) Wet chemical.

c) Standard deviation (SiO_2/Al_2O_3 = 0.15 K_2O/Al_2O_3 = 0.03). 10)
(*) at SiO_2/Al_2O_3 = 8.65.

the wet chemical techniques was difficult to define due to complexity of the procedures and lack of an extensive data base.

Table 2 shows good agreement for SiO_2/Al_2O_3 and alkali metal oxide/alumina ratios for various zeolites as measured by both ICPES (Direct) and various other techniques. Samples A, B, and C are offretite zeolites (with "theoretical" K_2O/Al_2O_3 ratios of 1.0, 0.75, and 0.25 respectively 9)) and show that excellent agreement exists between AAS/fusion and ICPES (Direct) data for both SiO_2/Al_2O_3 ratio and K_2O/Al_2O_3 ratios. Further, both techniques provide the expected K_2O/Al_2O_3 ratios reported in the literature. 9) Samples D, E and F (offretites) illustrate the variation in both K_2O/Al_2O_3 and SiO_2/Al_2O_3 ratios measurement when performed by four different techniques. Excellent agreement between ICPES (Direct) and the other techniques is obtained.

Samples G and H (offretites) illustrate that the uncertainty in the measurement of SiO_2/Al_2O_3 ratio as this increases above $\approx$ 10:1 becomes significant when determined via AAS/fusion (or ICPES/fusion) due to a decrease in the precision of Al measurement. By ICPES (Direct), the error involved in such a measurement can be controlled to $\approx \pm$ 0.15. Samples J-Q are various sodium zeolites (J, K (mazzites), L, M (mordenites) and N-Q (faujasites) and the data for these samples shows that again excellent agreement between the various techniques can be obtained for zeolites of these types. It will be noted, however, that in the case of the faujasite samples N-Q, data obtained by ICPES (Direct), although agreeing well with the wet chemical data shows SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios lower than those from the wet chemical method. No rationale can be offered to explain this at this time.

A parallel study shows that very large errors in both ratios can arise (from occluded, x-ray amorphous, water soluble sodium silicates) when analyzing the majority of sodium zeolites with a water carrier. 10)

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