Quantitative Multi-element Analysis of Denitration Ceramics by X-ray Fluorescence Spectrometry

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A procedure for the determination of C, Na, Mg, Al, Si, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, Ga, As, Se, Zr, Mo, Sb, La, Tl, Pb and Th based on two X-ray fluorescence (XRF) methods and combined with instrumental neutron activation analysis and infrared combustion analysis was developed to give quantitative analytical information on a large number of ceramic catalyst samples used for the denitration of flue gas from a coal-fired power plant. A special sample preparation method for small amounts (20 mg) of powder was used for XRF analysis. Two types of synthetic calibration standards were prepared: (1) single-element standards with an Fe_2O_3 matrix for the minor elements and limited concentration ranges (nine elements) and (2) multi-element standards with simulated matrices for the major elements and large concentration ranges (ten elements). The quantitative evaluation of minor elements was performed with a linear calibration graph. Major elements were determined using the so-called fundamental parameters program.

Keywords: *X-ray fluorescence spectrometry; ceramic denitration catalysts; fundamental parameters program*

Ceramic materials composed of oxides of iron are used for the "selective catalytic reduction"[1] with ammonia of nitrogen oxides (NO_x) in flue gases emitted from coal-fired power plants. Special forms of ceramic catalysts have been developed which allow the small dust particles of the flue gas to pass through them.[2]

This paper describes a scheme of analysis designed to investigate the behaviour of these ceramic materials during the denitration process and to record the changes in chemical composition caused by exposure to flue gases. It is expected that some of these changes will influence the effectiveness of the catalysts. No previous analytical work has been carried out in this field.

It was necessary to obtain information on a number of major, minor and trace elements within relatively short times, as the analysis of a large number of samples was needed. Non-destructive analytical methods were favoured, as the application of digestion or leaching procedures during the sample preparation could cause losses of some of the elements, *e.g.*, volatile elements, that could be expected to be accumulated on the surface of the ceramic materials.

The procedure described is based on X-ray fluorescence (XRF) spectrometry and instrumental neutron activation analysis (INAA). The emphasis lies on the XRF determinations; INAA measurements were mainly carried out for purposes of control.

The qualitative information needed to plan the quantitative measurements was obtained by qualitative XRF spectrometry and scanning electron microscopy in conjunction with energy-dispersive X-ray spectrometry (SEM - EDX). Samples were also analysed by infrared (IR) combustion spectrometry for the determination of carbon and sulphur.

Experimental

Instrumentation

The XRF measurements were made on a Rigaku S/MAX sequential wavelength-dispersive X-ray spectrometer, using the Dataflex 360B software (Rigaku USA, Danvers, MA, USA). The spectrometer was fitted with a 2.7-kW Rh

end-window tube (Machlett), which is normally operated at 50 kV and 50 mA. Samples were fixed on holders of diameter 4 cm. The area excited by XRF was approximately 3 cm in diameter.

The spectrometer was operated under a vacuum of 0.1 Torr, necessary to prevent excessive absorption of soft X-rays between Na Kα and Ca Kα.

INAA was used to analyse samples by the so-called "monostandard"[4] or "single comparator"[5,6] method. Samples were irradiated with thermal neutrons for 1 h in the DIDO Research Reactor (FRJ2) at Kernforschungsanlage Jülich, and Zr wires were used as neutron flux monitors. Samples were counted by conventional γ-ray spectrometry after cooling intervals of 5, 10 and 45 d after irradiation.

The elements determined by XRF were Al, As, Ca, Cr, Fe, K, Mg, Mn, Mo, Pb, S, Si, Ti, Tl, V, Zn and Zr and by INAA As, Co, Cr, Fe, Ga, La, Na, Sc, Se, Sb, Th and Zn.

A scanning JEOL-JSM 840 electron microscope (acceleration voltage 15 keV) was used for qualitative SEM - EDX measurements. Non-conductive samples were coated with carbon by means of a "sputter-coating" procedure and fixed on aluminium sample holders.

A LECO CS-344 sulphur and carbon combustion analyser was used for carbon and sulphur determinations. The sample was combusted in a stream of oxygen at approximately 1350 °C and the amounts of CO_2 and SO_2 evolved were measured in an IR cell. This well tested method was used to control the sulphur results obtained by XRF spectrometry.

Sampling

Three different types of ceramic catalyst materials, consisting mainly of a mixture of iron oxides (FeO and Fe_2O_3), were investigated: type A, iron oxides mixture without additives; type B, iron oxides mixture with Cr_2O_3 as additive; and type C, iron oxides mixture with V_2O_5 as additive. Al, Si and S compounds were also present as major components in all three types.

Plates (15×15×0.25 cm) of these ceramic materials, filling a fixed-bed reactor, were exposed to the flue gas emitted from

the burner of a coal-fired power plant. The flue gas, having a temperature between 350 and 400 °C and containing approximately 30 g m^{-3} of fly ash, was passed through the reactor at a maximum rate of 1200 m^3 h^{-1}. Samples of each type were taken after different exposure times, varying between several hundred and several thousand hours.

Preparation of Samples

Samples for qualitative analysis by XRF spectrometry or SEM were not ground but presented as pieces of the ceramic plates taken from the fixed-bed reactor. Hence, qualitative data represent principally the composition of surface layers of the samples.

Samples for quantitative analysis by XRF spectrometry were first crushed to a fine powder using an agate mortar and then a RETSCH/MS micromill. The grain size was checked with an optical microscope after the milling procedure. Grain sizes of 1.3 ± 0.5 μm were achieved. The pulverised samples were stored in desiccators (P$_2$O$_5$).

It was not necessary to pulverise samples for analysis by INAA. Pieces of the ceramic plates, approximately 1 × 1 cm in size, were each packed in high-purity Al foil. Batches of 10–12 such samples were packed with zirconium wires (used as neutron flux monitors) into aluminium irradiation capsules. These capsules were irradiated under the conditions already mentioned.

Sample Preparation for XRF Analysis

A special sample preparation method for XRF analysis has been described recently.[3] It consists chiefly in glueing small amounts of fine powder (20 mg) on filter-paper (see Fig. 1).

Below the sample and its support is a PTFE beaker that serves as a radiation trap. The powder is glued on to the filter-paper by means of nail polish prepared by dissolving 0.55 g of collodion cotton (10 g nitrogen per 100 g of nitrocellulose) in a mixture of 3.3 ml of butyl acetate, 1.1 ml of ethyl acetate and 50 μl of dibutyl phthalate. A 100-μl volume of this nail

polish is mixed with 20 mg of the powder sample, glued to the filter-paper and dried for 10 min at 70 °C. Such samples can be irradiated by X-rays for 2 h *in vacuo* at 50 kV and 50 mA without major radiation damage and without contamination of the spectrometer.

Preparation of Standards

For the determination of minor elements by XRF spectrometry, a series of single-element synthetic calibration standards was prepared for each element to be determined. Fe$_2$O$_3$ was used as the matrix component, to which different elements were added in the form of common laboratory-reagent grade compounds chosen to satisfy the following criteria: the compound has to be stoicheiometric, hard and brittle (necessary for satisfactory mixing during the milling procedure) and already fine enough before milling.

The compounds were milled in a ball-mill under well-tested conditions.[7] The standards were prepared by mixing the pre-ground compounds in a micromill.

Table 1 gives the standard series that were prepared in this way. The theoretically required grain sizes, d (last column), were calculated from the linear absorption coefficient, μ, of the fluorescence lines of the elements for an Fe$_2$O$_3$ matrix[8] using the equations

$$d = 0.2 \, \mu^{-1} \qquad \ldots \quad \ldots \quad \ldots \quad (1a)$$

and

$$\mu = \rho \times \frac{2A_{Fe}(\mu/\rho)_{Fe} + 3 A_{O}(\mu/\rho)_{O}}{M} \qquad \ldots \quad \ldots \quad (1b)$$
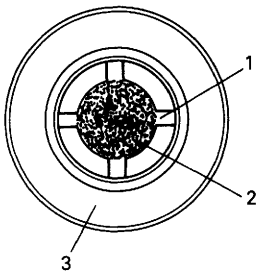

Fig. 1. Sample preparation on a filter-cross, X-rays from above, half actual size: 1, arms of the filter-cross; 2, centre of the filter-cross, covered with 20 mg of powder and nail polish; and 3, mask
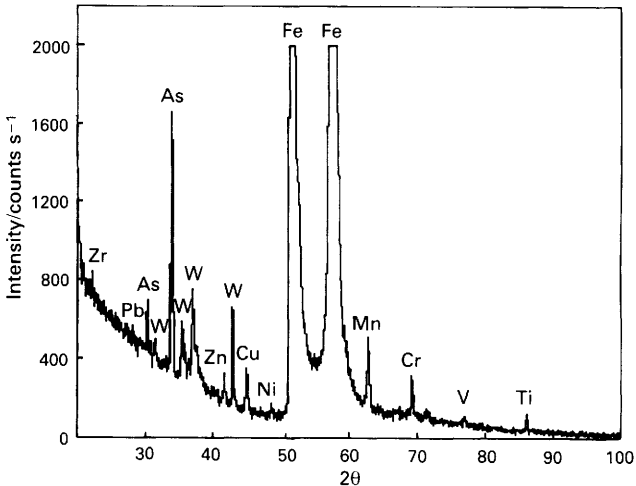

Fig. 2. X-ray spectrum of 20 mg of ground powder sample of loaded ceramic AII2 measured on the S/MAX sequential spectrometer using a Rh end-window tube (50 kV, 50 mA), LiF (200) analyser crystal, step width 0.05°, counting time 1 s, coarse collimator. W is contamination from the milling vessel

Table 1. Calibration standards prepared for single elements for minor concentration ranges, and for XRF analysis n standards were prepared with $c = A + BI$ (c = concentration, I = intensity). The concentration is given in μg g^{-1}; A and the standard deviation have the same dimension. The intensity is given in counts s^{-1}, and consequently B has the dimensions μg g^{-1} counts^{-1} s (reciprocal sensitivity); t (s) is the counting time. The matrix was finely ground crystalline Fe$_2$O$_3$ powder. The required grain size d (10^{-6} m) is given in the last column; μ is the linear absorption coefficient. Further explanations are given in the text

Element			Compound	n	Concentration range	t	A	B	σ	$d=0.2/\mu$
Ti	..	..	TiO$_2$	6	30–178	200	−16	5.31	11	2.5
V	..	..	V$_2$O$_5$	6	50–300	200	6	1.60	5	3.1
Mn	..	..	KMnO$_4$	6	17–105	200	5	0.55	3	5.2
Zn	..	..	ZnO	6	36–220	200	−421	1.63	24	2.1
As	..	..	As$_2$O$_3$	4	2000–10000	40	163	5.57	260	4.7
Zr	..	..	ZrO$_2$	6	50–300	200	36	0.92	5	10.9
Mo	..	..	MoO$_3$	7	50–500	40	20	0.88	15	14.8
Tl	..	..	TlCl	5	200–1000	100	44	5.71	61	5.3
Pb Lβ$_1$		..	PbO	7	50–500	40	−194	3.24	22	5.8

Table 2. Semi-quantitative surface composition (mass-%) averaged over n samples of three different types of ceramics. These data were obtained by SEM - EDX

Oxide			Type A ($n = 14$)	Type B ($n = 9$)	Type C ($n = 4$)
Al_2O_3	..	..	2.9	5.8	5.2
SiO_2	..	..	7.4	8.8	8.2
SO_3 ..	..	..	5.0	2.3	1.5
K_2O	..	..	1.1	0.8	0.7
CaO	..	..	1.2	0.8	0.6
TiO_2	..	..	0.8	0.3	0.2
V_2O_5	..	..	0	0	0.9
Cr_2O_3	..	..	0	1.7	0
Fe_2O_3	..	..	79.2	77.1	78.1
As_2O_3	..	..	2.4	2.4	4.6

ρ is the density of Fe_2O_3, M is the relative molecular mass of Fe_2O_3 and A is the relative atomic mass.

For the determination of major and some minor elements by XRF spectrometry, a series of six multi-element synthetic calibration standards, simulating the matrices of all three types of ceramic samples, were prepared. For this purpose, the semi-quantitative data in Table 2 obtained by means of SEM - EDX analysis were used to define the elemental concentration ranges of the six synthetic standards. The selection of the chemical compounds and the whole preparation process followed the scheme already described for single-element standards. The only difference here was that, after milling, the powders were mixed using a ball-mill rather than a high-speed micromill because of the large number of compounds that had to be mixed.

The compositions of all six synthetic standards are given in Table 3.

Results

Qualitative Results

Qualitative XRF measurements on ceramic samples led to the detection of the major elements (Al, Si, S or Fe) and also the minor elements (Ti, Mn, Zn, As, Zr, Mo, Tl, Pb and others). These elements were identified by interpretation of X-ray spectral scans such as that in Fig. 2.

Fig. 3 compares the SEM - EDX spectra of a fresh and a used ceramic material. SEM - EDX measurements could therefore give semi-quantitative information about Al, Si, S, K, Ca, Ti, V, Cr, Fe and As.

Quantitative Results

Quantitative XRF analyses for minor elements over limited concentration ranges were based on the construction of a calibration graph for each element, calculated as a linear correlation between the net fluorescence intensities and the concentration of a series of single-element standards. These calibration graphs were used to determine the concentrations of Ti, V, Mn, Zn, As, Zr, Mo, Tl and Pb from the respective net intensities in the samples.

Table 1 gives information on the coefficients A and B of the calibration graphs for each element and Fig. 4 shows such a graph for Mn.

A different software procedure, the so-called "fundamental parameters program," was used for the quantitative XRF analysis of major and some minor elements over large concentration ranges. Theoretical predictions of X-ray intensities were calculated using the XRF-11 software package.[9] These predictions were required, together with measured intensities from a few standards, in order to determine the chemical composition of homogeneous samples analysed by XRF spectrometry. The theoretical intensity predictions were made according to the fundamental parameters method.[10,11]

The results are presented in Tables 4 and 5. INAA was used for Na, Se and Sb, which may be relevant for the denitrifica-
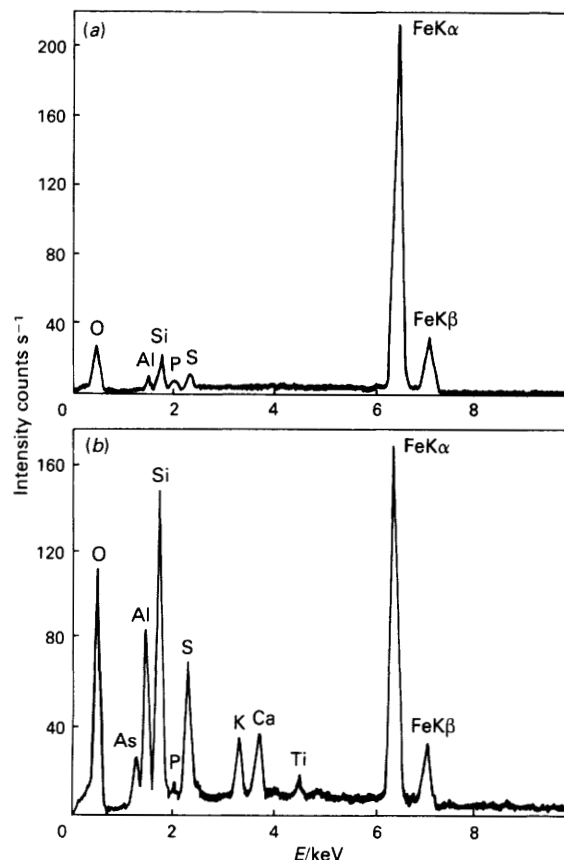

Fig. 3. Energy-dispersive X-ray spectra showing the surface composition of two pieces of ceramic plate, measured on a scanning electron microscope: (*a*) fresh ceramic AII0; and (*b*) loaded ceramic AII² (As Lα_1 + As Lβ_1) is seen left of Al Kα; As Kα (10.53 keV) is outside the range of this spectrum
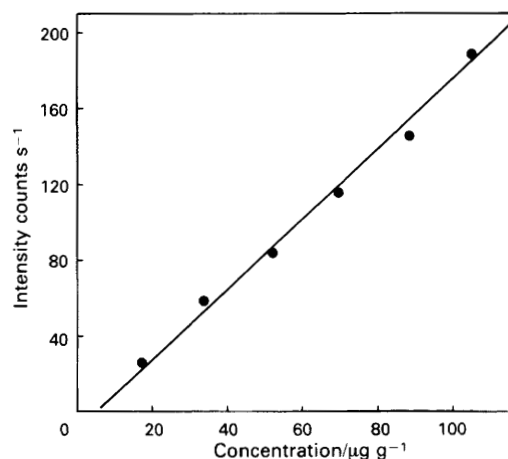
Fig. 4. Regression line $c = 5.15 + 0.546\ I$ [c = concentration, I (intensity) = count rate] for Mn from six artificial standards, derived from mixtures of $KMnO_4$ and Fe_2O_3 (matrix). This is the graphical representation of line 3 in Table 2. Measurement times were 100 s on a Kα line, background left and background right

tion of flue gases, and for the trace elements Sc, Co, Ga, La and Th. Chromium, Fe, Zn and As were determined by both INAA and XRF.

In total 26 elements were determined quantitatively. One can classify these elements with respect to their enrichment in ceramic samples exposed to flue gas into three groups.

1. Elements that are strongly enriched: As, Mo, Sb and Tl.
2. Elements that are only slightly enriched: Zn, Se, Zr and Pb.
3. Elements that remain unchanged: C, Na, Mg, Al, Si, S, K, Ca, Sc, Ti, V, Cr, Fe, Mn, Co, Ga, La and Th.

Table 3. Compositions of the six synthetic standards used for the fundamental parameters analysis (concentrations in g per 100 g). The "found" values were obtained by making a second measurement with the standards as unknowns. The total of the oxides is is never 100 mass-% because of unanalysed water of crystallisation in $CaSO_4.2H_2O$ and surplus oxygen in $K_2Cr_2O_7$.

Oxide	Compound	Standard I Given	Found	Diff.	Standard II Given	Found	Diff.	Standard III Given	Found	Diff.	Standard IV Given	Found	Diff.	Standard V Given	Found	Diff.	Standard VI Given	Found	Diff.
MgO	MgO	1.08	1.08	0	1.00	0.96	−0.04	2.00	2.01	+0.01	1.40	1.36	−0.04	0.00	0.00	0	1.80	1.75	−0.05
Al_2O_3	Al_2O_3	3.00	3.10	+0.10	4.42	4.36	−0.06	7.00	7.04	+0.04	8.00	7.95	−0.05	6.00	6.05	+0.05	6.52	6.52	0
SiO_2	SiO_2	10.00	10.17	+0.17	11.00	10.83	−0.17	12.14	12.19	+0.05	8.00	8.03	+0.03	7.97	7.91	−0.06	7.00	6.92	−0.08
SO_3	$CaSO_4.2H_2O$	0.90	1.01	+0.11	1.50	1.66	+0.16	2.26	2.51	+0.25	5.26	5.85	+0.59	3.76	4.20	+0.44	1.93	2.17	+0.24
K_2O	$K_2Cr_2O_7$	1.20	1.20	0	0.68	0.68	0	1.00	1.01	+0.01	0.68	0.70	+0.02	0.00	0.00	0	0.80	0.79	−0.01
CaO	$CaSO_4.2H_2$	0.64	0.71	+0.07	1.06	1.14	+0.08	1.59	1.74	+0.15	3.71	4.20	+0.49	2.65	2.85	+0.20	1.36	1.48	+0.12
TiO_2	TiO_2	0.00	0.00	0	0.20	0.20	0	0.40	0.39	−0.01	0.60	0.62	+0.02	0.80	0.79	−0.01	1.00	0.99	−0.01
V_2O_5	V_2O_5	0.22	0.23	+0.01	0.00	0.00	0	0.46	0.45	−0.01	0.00	0.00	0	1.10	1.08	−0.02	0.00	0.00	0
Cr_2O_3	$K_2Cr_2O_7$	1.94	1.92	−0.02	1.10	1.10	0	1.61	1.63	+0.02	1.10	1.10	0	0.00	0.00	0	1.29	1.28	−0.01
Fe_2O_3	Fe_2O_3	80.00	81.29	+1.29	78.00	77.40	−0.60	70.00	69.75	−0.25	68.49	69.30	+0.81	76.00	75.79	−0.21	77.00	76.20	−0.80
Total		99.0	100.7	+1.7	99.0	98.3	−0.7	98.5	98.7	+0.2	97.3	99.1	+1.8	98.3	98.7	+0.4	98.7	98.1	−0.6

Table 4. Concentrations of major elements in the ceramics (italic figures, g per 100 g; roman figures, $\mu g\ g^{-1}$. RA = XRF type 1 analysis; FP = XRF type 2 analysis defined in the summary; IR = infrared combustion analysis; NA = neutron activation analysis; n.d. = not determined). The sample designations characterise different types of ceramics (A, B, C), different reactor loadings (I, II, III) and different exposure times to the flue gas (0, 1, 2, 3). σ is the standard deviation of the method

Sample designation	Mg FP	Al FP	Si FP	S FP	S IR	K FP	V RA	V FP	Cr FP	Cr NA	Fe FP	Fe NA
AI0	0	0.34	2.32	0.73	0.94	15	20	19	22	16	64.08	62.57
AI2	94	0.41	2.08	500	600	297	82	105	60	21	60.49	62.97
AII0	0	1.40	3.76	0.94	0.95	924	24	34	252	150	64.50	58.62
AII1	0	1.12	3.03	1.15	1.26	1100	29	45	290	223	60.53	55.71
AII2	0	1.11	2.93	1.26	1.28	1100	33	44	340	259	60.96	57.18
BI2	1.87	1.01	1.41	1.39	1.29	0	98	161	7.31	7.90	54.98	n.d.
BII1	1.04	0.63	1.81	1.18	1.33	0	59	95	2.87	3.79	65.80	n.d.
BII3	1.11	0.75	2.18	1.24	1.38	715	87	141	2.92	2.94	60.20	54.78
CI3	0	1.41	3.30	0.79	0.94	945	n.d.	1.45	105	105	59.36	57.17
σ	0.04	0.03	0.07	0.03	0.05	13	5	6	5	2	1.92	0.09

Element and method

Table 5. Concentrations of minor and trace elements in the ceramics (μg g^{-1}). Details as in Table 4

Sample desig-nation	C IR	Na NA	Ca FP	Sc NA	Ti RA	Ti FP	Mn RA	Co NA	Zn RA	Zn NA	Ga NA	As RA	As NA	Se NA	Zr RA	Mo RA	Sb NA	La NA	Tl RA	Pb RA	Th NA
AI0 ..	100	61	195	1	233	191	169	2	0	13	0	0	0	2	0	0	0	5	0	0	0.5
AI2 ..	0	105	281	1	302	246	178	3	78	n.d.	2	1099	629	5	0	32	16	5	106	13	0.6
AII0 ..	80	88	183	2	599	422	191	3	0	0	3	0	0	0	0	0	0	8	0	0	1.6
AII1 ..	110	137	245	2	498	423	208	3	0	91	4	1540	1204	19	0	43	6	7	0	0	1.7
AII2 ..	230	142	244	2	525	438	242	3	82	n.d.	5	2168	1430	27	47	62	14	7	62	0	1.5
BI2 ..	100	45	331	3	339	368	222	54	94	99	7	0	251	12	35	27	2	3	0	0	0.4
BII1 ..	190	81	322	2	297	321	197	22	0	40	4	546	965	8	16	0	6	4	0	0	0.6
BII3 ..	0	202	426	2	353	320	240	18	149	n.d.	7	5999	4558	9	22	324	61	4	247	0	0.5
CI3 ..	70	111	206	1	410	424	158	2	86	n.d.	6	10665	7230	7	127	232	67	7	372	25	1.9
σ ..	50	0.2	9	0.01	11	10	3	0.01	24	10	2	260	12	2	5	15	0.3	0.05	61	22	0.4

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