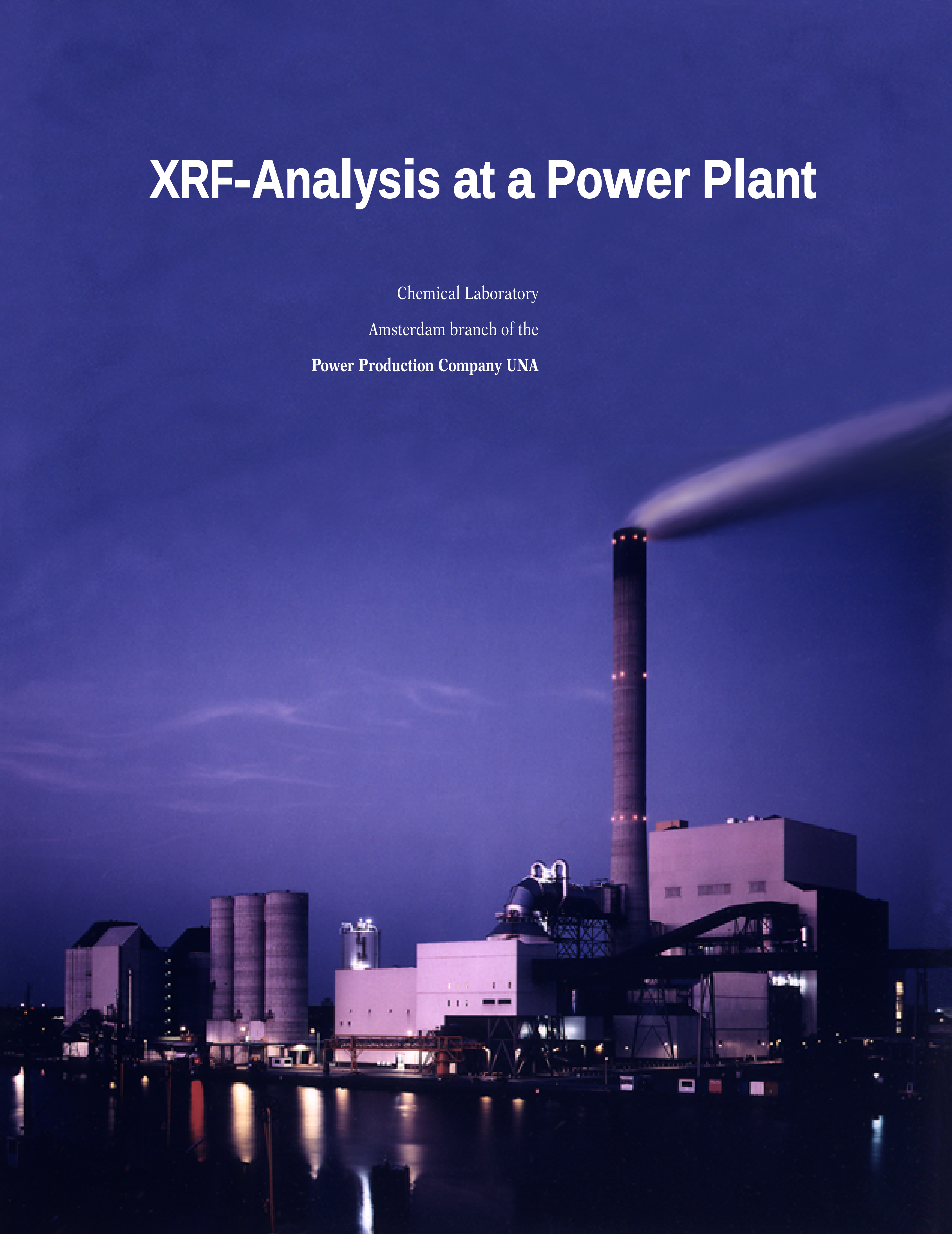
XRF-Analysis at a Power Plant

Chemical Laboratory
Amsterdam branch of the
Power Production Company UNA



XRF Analysis at a Power Plant

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Introduction

The Power Production Company UNA operates 6 power stations at various locations in the Netherlands, one of which is Amsterdam. For environmental and economical reasons, there are strict procedures for checking and controlling the quality of materials, such as water, fuels, lubricants, rest materials and sewage.
This routine work is carried out by 3 laboratories.

The power plant at Amsterdam has 2 power units, one of 520 MW powered by natural gas, the other generates 630 MW and is powered by coal. The rest materials of the latter are sold for use in construction. The quality of these materials, being mainly fly ash, sediment ash and gypsum, must of course satisfy customer requirements.

Adding Sewage Sludge to Coal

In 1995, our laboratory in Amsterdam participated in a research project to investigate the feasibility of adding sewage sludge to the coal. This would solve the problem of disposing the sludge that comes from the sewage cleaning plant of the city of Amsterdam. In January 1995, we started to try and mix an increasing amount (1 to 6%) of sewage sludge in the power station's coal. A study was made of effects on burning and on the quality of the fume gases and rest materials. The results were satisfying. It is now routine practice to add sewage sludge to the fuel.
For the sewage sludge project, a program was defined for elemental analysis of fuels, sludges and rest materials. This program was made and carried out in co-operation with the Dutch institute, KEMA. It includes the determination of traces of V, Cr, Mn, Co, Cu, Zn, As, Se, Mo, Cd, Sn, Sb, Te, Ba, Hg and Pb.
KEMA analysed by means of OES- ICP, whilst we analysed the same samples by XRF with the UniQuant® method/program. Comparative results are presented at the end of this note.

X-Ray Fluorescence (XRF) Analysis

The major part of our routine samples are analysed by XRF because it can directly work with solid samples. In addition, we have an AAS-HGA for analysing traces in solid samples at levels which are below the detection limit of XRF.
To be noted that analysing by OES-ICP would require that solid samples are first converted to a liquid, which is a time consuming process.

Most samples for XRF are either pressed to a pellet (disc shaped) or are converted to a homogeneous glass disc (the bead) by fusion with Lithium Tetraborate.
The fused bead technique overcomes heterogeneity effects and is generally required for obtaining highest analytical accuracies for minors and majors, in particular for silicon oxide and iron oxide. On the other hand, pressed pellets are more suitable for trace analysis. The pellets are either pressed in its undiluted form or are first mixed with a binder, 7.5 gram sample + 1.5 gram 'Hoechst Wax C'. This small dilution still ensures high X-Ray intensities as required for trace analysis. Unlike with fusions, the volatile elements remain in the prepared specimen, the pressed pellet.
Here is an overview:

Sample	**Sample preparation**
Coal (Sulphur content)	Pressed pellet
Coal ash	Fused bead (1 sample + 7 $Li_2B_4O_7$)
Limestone	Pressed pellet with some binder (Boric acid)
Water treatment sludge	Pressed pellet
Slurry gypsum	Pressed pellet

In addition there is a large variety of occasional samples, such as steel, brass, furnace scale, cool water sludge and soil samples. Details of sample preparation of 'power plant routine samples' will be included in the next edition of the UniQuant manual.

Our XRF spectrometer is of the type X'Unique manufactured by Philips. It includes the software X40 that we mainly use to control the spectrometer in a way as prescribed by the UniQuant® method/program, see next section.

UniQuant®

UniQuant® is a PC program that has been developed by W.K. de Jongh and W.J. de Jongh of Omega Data Systems b.v.
We use the UniQuant® method/program extensively for the following reasons:

- Our analyte samples are of very different natures. Usually, no standards are available. UniQuant® can work without standards.

- One and the same analytical measuring program is used for all kinds of samples.

- One and the same initial (one-off) calibration is used for all samples.

- Data evaluation is transparent and fast so as to allow good interactivity. If required, recalculations can be made later, perhaps on the basis of additional information such as about any organic rest in the sample.

- Because of its ease of operation, UniQuant® can be routinely used by all laboratory personnel.

- The analytical accuracies are as required.

- For each reported concentration, UniQuant® also reports an estimated confidence interval by means of a StdErr, see tables. The StdErr is calculated on the basis of counting statistics, on the extent of corrections made for background and spectral line overlaps and on a factor that reflects practical experience.

Research on Traces in Sewage Sludge

Both OES-ICP and XRF/UniQuant® were used for trace analysis. In this study, a mass balance had to be made for the complete system of in- and outgoing materials. This required the determination of trace elements at levels below the detection limit of XRF. As a consequence, the OES-ICP method was indispensable. However all samples were also analysed by XRF/UniQuant® in order to learn about its capabilities. We found a good agreement between the results by OES-ICP and XRF/UniQuant® for traces that are above the limit of determination.
The following conclusions could be made regarding XRF/UniQuant®.

- The method is suitable for trace analysis in quality control where for the lowest traces it is adequate to certify that they are lower than 10 mg/kg.

- The method is cost saving. Since XRF is a multi-element method, it is much faster than the AAS-HGA in our lab. Costs are lower then when making use of external facilities.

- Batches of samples for trace analysis are run overnight, thus not interfering with our daily routine work.

- UniQuant® evaluates research samples in the same way as the routine samples.
UniQuant® is based on the calibration of instrumental sensitivities, Kappas, which are independent of samples. The calculation of concentrations from X-Ray intensities assume that the samples are homogeneous. If they are not, like is often the case for power samples, the analytical accuracy is adversely affected. This problem is largely overcome by firming up UniQuant's Kappas by means of one or a few standards that have the same physical nature as the analyte samples. For this reason we used standards such as CTA-FFA1, ASCRM-010, NBS 1633a, ECO and ECH.
The measuring times for the trace elements were set longer then UniQuant's usual 6 or 10 seconds per element, for example 20, 40 or 60 seconds.

Conclusions

- The XRF/UniQuant® results compare well with those of ICP.
Although the Kappas (instrumental sensitivities) are firmed up by means of fly ash standards, when applied to coal samples, the results are still very close to those obtained by ICP.

- Because traces below 10 mg/kg can be ignored in our quality control, XRF/UniQuant® can be used instead of OES-ICP.
The advantage with respect to ICP is that sample preparation is far less elaborate.

- The use of the XRF+UniQuant® method is recommended for laboratories of power plants.

Coal

UNA #1 as pressed pellet

	XRF/UniQuant®		OES/ ICP	
	Conc.	StdErr	Conc.	StdErr
V	24	1	25.7	1.3
Cr	16	1	25.9	1.3
Mn	98	5	95	5
Co	7	1	5.4	0.4
Ni	15	1	20.1	1.9
Cu	10	1	8.9	0.3
Zn	30	2	23.0	1.1
As	< 10	5	4.8	0.4
Se	< 2	1	< 0.9	
Mo	< 6	3	3.01	0.20
Cd	< 10	5	0.054	0.005
Sn	< 10	5	< 2.0	
Sb	< 10	5	< 1.5	
Te	< 10	5	< 0.9	
Ba	150	10	227	
Hg	< 4	2	0.081	0.008
Pb	< 10	5	6.8	0.9

Sediment Ash

UNA #2 as pressed pellet

	XRF/UniQuant®		OES/ ICP	
	Conc.	StdErr	Conc.	StdErr
V	161	8		
Cr	174	9	160	8
Mn	1070	50		
Co	36	4		
Ni	91	5	93	11
Cu	210	10	220	11
Zn	375	20	383	25
As	< 12	6	8.8	1.4
Se	< 2	1	< 4	
Mo	< 6	3		
Cd	< 10	5	0.53	0.05
Sn	18	5		
Sb	< 10	5		
Te	< 10	5		
Ba	1715	70		
Hg	< 4	2	< 0.06	
Pb	105	6	94	6

Fly Ash

UNA #3 as pressed pellet

	XRF/UniQuant®		OES/ ICP	
	Conc.	StdErr	Conc.	StdErr
V	220	10		
Cr	130	7	143	7
Mn	495	20		
Co	48	4		
Ni	116	6	110	12
Cu	240	10	242	12
Zn	330	20	306	20
As	35	7.0	33	3
Se	3	1	< 4	
Mo	< 6	3		
Cd	< 10	5	0.76	0.06
Sn	< 10	**5**		
Sb	< 10	5		
Te	< 10	5		
Ba	1700	70		
Hg	< 4	2	< 0.06	
Pb	121	6	112	4

Fly Ash

UNA #4 as pressed pellet

	XRF/UniQuant®		OES/ ICP	
	Conc.	StdErr	Conc.	StdErr
V	178	9		
Cr	87	5	81	4
Mn	840	40		
Co	39	3		
Ni	94	5	88	12
Cu	182	10	178	9
Zn	370	20	336	21
As	22	7	21.1	2.0
Se	< 2	1	< 4	
Mo	< 6	3		
Cd	< 10	5	0.80	0.06
Sn	< 10	5		
Sb	< 10	5		
Te	< 10	5		
Ba	1710	70		
Hg	< 4	2	< 0.06	
Pb	110	6	99	4

CTA-FFA1

as bead (1 sample + 7$Li_2B_4O_7$)

	XRF/UniQuant®		Certificate	
	Conc.	StdErr	Conc.	StdErr
V	210	10	260	10
Cr	150	8	156	8
Mn	1170	50	1066	41
Co	46	6	39.8	1.7
Ni	101	7	99	5.8
Cu	172	9	158	9
Zn	650	30	569	58
As	< 80	40	53.6	2.7
Se	< 12	6	4.6	
Mo	< 40	20	17	
Cd	< 40	20	2.8	
Sn	< 60	30		
Sb	< 60	30	17.6	2.5
Te	< 80	40		
Ba	600	80	835	56
Hg	< 40	20		
Pb	510	30	369	46

as pressed pellet

	XRF/UniQuant®		Certificate	
	Conc.	StdErr	Conc.	StdErr
V	240	10	260	10
Cr	154	8	156	8
Mn	1040	50	1066	41
Co	36	3	39.8	1.7
Ni	97	5	99	5.8
Cu	162	9	158	9
Zn	610	30	569	58
As	61	7	53.6	2.7
Se	5	1	4.6	
Mo	10	3	17	
Cd	10	3	2.8	
Sn	< 10	5		
Sb	19	6	17.6	2.5
Te	< 12	6		
Ba	770	40	835	56
Hg	< 4	2		
Pb	500	30	369	46

All data are in mg/kg (ppm)

Sewage Sludge

an arbitrary routine sample from the Amsterdam sewage cleaning plant as analysed by XRF/UniQuant® on a pressed pallet

	CConc.	StdErr
	Mass%	Mass%
Na_2O	0.30	0.02
MgO	0.79	0.02
Al_2O_3	5.21	0.07
SiO_2	8.38	0.09
P_2O_5	8.16	0.08
SO_3	4.97	0.06
Cl	0.134	0.006
K_2O	0.27	0.01
CaO	7.09	0.08
TiO_2	0.29	0.01
Fe_2O_3	6.41	0.07
Organic	57.5	
	mg/kg	mg/kg
V	8	2
Cr	51	3
Mn	430	20
Co	12	2
Ni	34	2
Cu	450	20
Zn	990	50
As	< 12	6
Se	< 12	1
Br	53	3
Rb	7	2
Sr	450	20
Zr	63	8
Nb	< 12	6
Mo	< 6	3
Cd	< 10	5
Te	< 12	10
Sn	32	8
Sb	< 12	10
I	100	10
Cs	60	20
Ba	350	30
Hg	< 4	2
Pb	230	10

Typical compositions of Coal, Sediment Ash and Fly Ash

Concentrations are in %

	Coal	Sediment Ash	Fly Ash
Na_2O	0.04	0.46	0.38
MgO	0.13	1.09	0.96
Al_2O_3	3.22	20.6	25.4
SiO_2	6.96	53.3	52.2
P_2O_5	0.04	3.32	2.31
K_2O	0.15	0.99	1.60
CaO	0.42	6.34	3.96
TiO_2	0.16	1.22	1.36
MnO	0.013	0.14	0.069
Fe_2O_3	0.92	10.9	9.7
S	0.78		
SO_3		0.09	0.30
Cl	0.030	0.003	0.060
C	69.89	0.94	1.21
H	4.79	0.06	< 0.01
N	1.24	0.13	< 0.01
Moisture	4.0		

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