APPLICATION REPORT

XRF 179

ZSX PRIMUS SERIES

EVOLUTION FROM SEMIQUANTITATIVE ANALYSIS
PRINCIPLE AND APPLICATIONS OF SQX (SCAN QUANT X)

INTRODUCTION

The SQX (Scan Quant X) analysis can obtain rough concentrations directly from qualitative analysis (identification analysis) results without using standard samples (also called "in a standardless procedure"). Such analysis is generally known as "semiquantitative analysis".[1)] Only by entering information on whether an unknown sample is oxide or metal or information on components in glass bead flux or a polymer and by specifying analysis conditions, a qualitative analysis and a semiquantitative analysis are made automatically and analysis results can be obtained.

Keywords: SQX analysis, semiquantitative analysis, fundamental parameter method, standardless analysis, sensitivity library, sensitivity conversion library, shape correction

1. PRINCIPLE[2), 3)]

Fig.1 shows a flowchart of the analysis. Measurements and data processing are carried out in order of a continuous scan measurement, fixed angle analysis, counting loss correction, smoothing processing, peak search and background subtraction. After measurements are completed, an identification analysis is made immediately and an SQX analysis is carried out based on a correct identification result. The presence of overlaps is checked first and spectral lines on which overlaps have no or little effects are automatically selected. The intensities of measured spectral lines are compared with library intensities in the instrument and the influence of the absorption and enhancement of coexisting elements is corrected using the fundamental parameter method (FP method) to obtain final concentrations. The overlap correction is also made automatically when calculating concentrations. Since this overlap correction uses calculated theoretical intensities, the correction can be made properly regardless of a sample matrix and whether a sample is a bulk or a thin film. A series of these procedures are carried out automatically and continually.

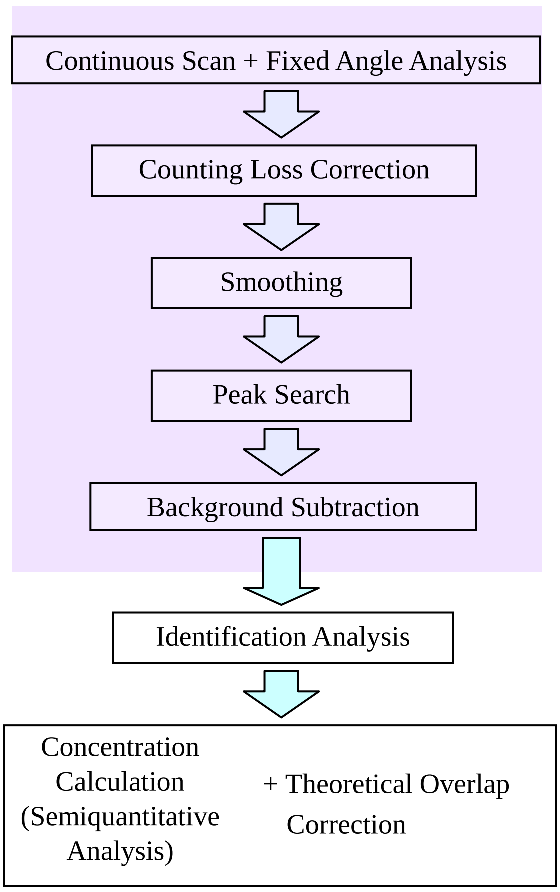


Fig.1 Flowchart of SQX Analysis

Elements that can be analyzed are 5B to 92U, though they vary depending on an analyzing crystal. The reason why the SQX analysis can make analyses without standard samples is that data libraries have been stored in the instrument. Data libraries consist of sensitivity libraries and sensitivity conversion libraries.

First, sensitivity libraries are explained. It is known that there is a constant correlation between an element and a sensitivity. For example, Fig.2 shows a plotted chart of the atomic numbers of Ti to Cu and the X-ray intensities of the pure substances of those elements. In this range, when the intensities of Ti, Cr, Fe and Cu are known as shown with the arrows, those of elements between Ti and Cu can be estimated using interpolation. By using this interpolation, for all elements from F to U, when the intensities of typical elements have been measured and registered beforehand, other elements can be analyzed without measuring their intensities.

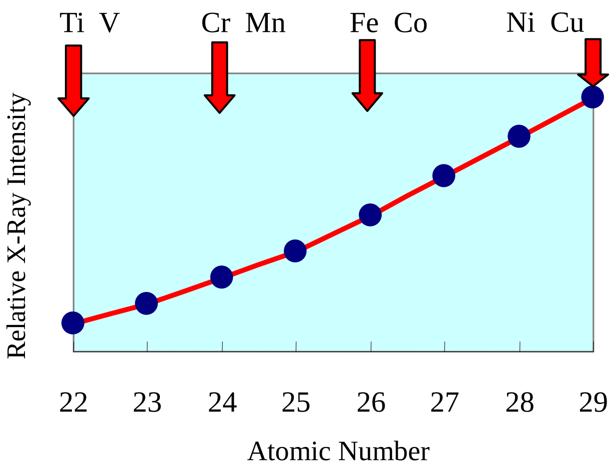


Fig.2 Correlation Between Element and Sensitivity

However, if a mask diameter is different for each sample or a measured spectral line overlaps with another, a sensitivity library must be registered each time. Re-registering takes time and is not a good method. To solve this problem, one sensitivity library has been registered as a standard condition and the instrument has parameters to convert measured intensities so that one library standard condition can be used even when a mask diameter or a measured spectral line is different. This is called a sensitivity conversion library. Since those parameters have been registered in the instrument, a user does not have to re-register them.

The SQX also has the “fixed angle measurement” function, which carries out fixed time counting at optimum peak angles and background angles for specified elements after a qualitative scan, and therefore semiquantitative analyses with higher precision are possible.[4)]

2. INSTRUMENT AND MEASURING CONDITIONS

Instrument : ZSX Primus II (ZSX Primus)

X-Ray Tube : Rh end window type tube

Measuring Conditions

<table>
<tr><td>Element</td><td>F - Mg</td><td>Al, Si</td><td>P, S</td><td>Cl</td><td>K, Ca</td><td>Ti - U</td></tr>
<tr><td>kV-mA</td><td colspan="4">30-100</td><td>40-75</td><td>50-60</td></tr>
<tr><td>Slit</td><td colspan="3">S4</td><td>S2</td><td>S4</td><td>S2</td></tr>
<tr><td>Analyzing Crystal</td><td>RX25</td><td>PET</td><td colspan="2">Ge</td><td>LiF200</td><td>LiF200</td></tr>
<tr><td>Detector</td><td colspan="5">PC</td><td>SC</td></tr>
<tr><td>PHA</td><td colspan="6">Differential mode</td></tr>
</table>

3. APPLICATIONS OF SQX ANALYSIS

3-1 ANALYSES OF SODA-LIME GLASS AND STAINLESS STEEL (APPLICATION TO BULK SAMPLES)

As examples of measurements of bulk samples, SQX analyses were made in an element range of F to U by using the soda-lime glass standard sample (NIST1631) and the stainless steel sample (JSS 652-11) as unknown samples. The measurement diameter was 30mm. Table 1 shows the analysis result of the soda-lime glass and Table 2 shows that of the stainless steel. Figs.3 and 4 show the whole angle qualitative charts of those samples. The measurement results are in good agreement with chemical analysis values from main components to trace elements.

In the analysis of stainless steel, Mo-L1 overlaps with the measured line P-Kα (see the chart in Fig.4). Since the SQX has the "theoretical overlap correction function", accurate analysis values can be obtained even for P in stainless steel containing 2 mass% of Mo without an analyst's special operation for the overlap of spectral lines.[5)]

Table 1 SQX Analysis Result of Soda-Lime Glass Standard Sample

Unit: mass%

Element	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO
Chemical Analysis Value	73.08	1.21	0.087	0.019	8.20
X-Ray Fluorescence Analysis	72.4	1.24	0.098	0.019	8.8
Difference	0.68	-0.03	-0.011	0	-0.6
Element	MgO	Na_2O	K_2O	SO_3	
Chemical Analysis Value	3.51	13.32	0.33	0.25	
X-Ray Fluorescence Analysis	3.72	13.1	0.34	0.25	
Difference	-0.21	0.22	-0.01	0	

Table 2 SQX Analysis Result of Stainless Steel

Unit: mass%

Element	Si	Mn	P	Ni
Chemical Analysis Value	0.40	1.71	0.030	11.15
Measurement Value	0.40	1.83	0.027	11.08
Difference	0	-0.12	0.003	0.07
Element	Cr	Mo	Cu	Co
Chemical Analysis Value	16.85	2.13	0.14	0.22
Measurement Value	17.16	2.22	0.13	0.23
Difference	-0.31	-0.09	0.01	-0.01

C was calculated as a fixed value.

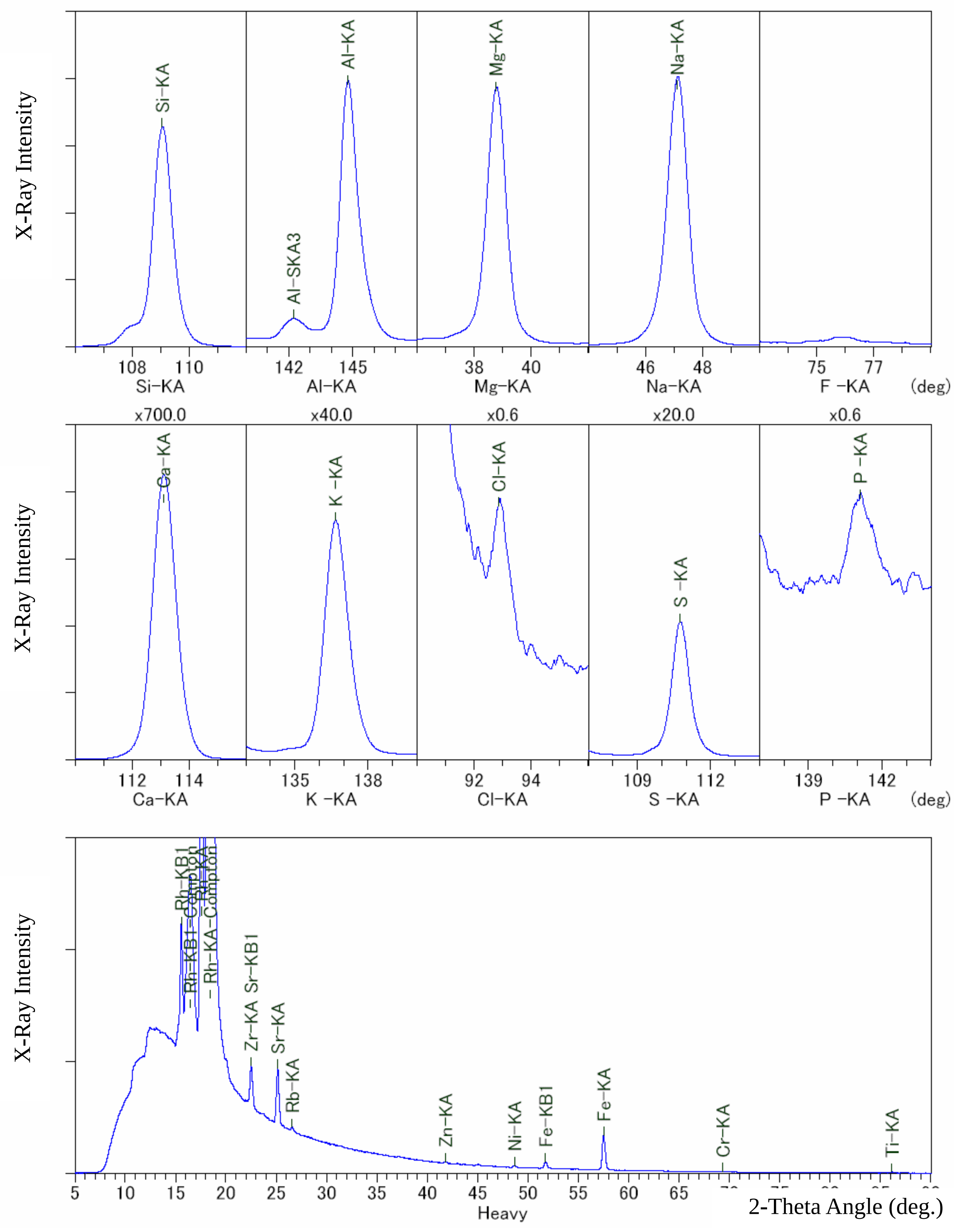


Fig.3 Whole Angle Qualitative Chart of Soda-Lime Glass Standard Sample

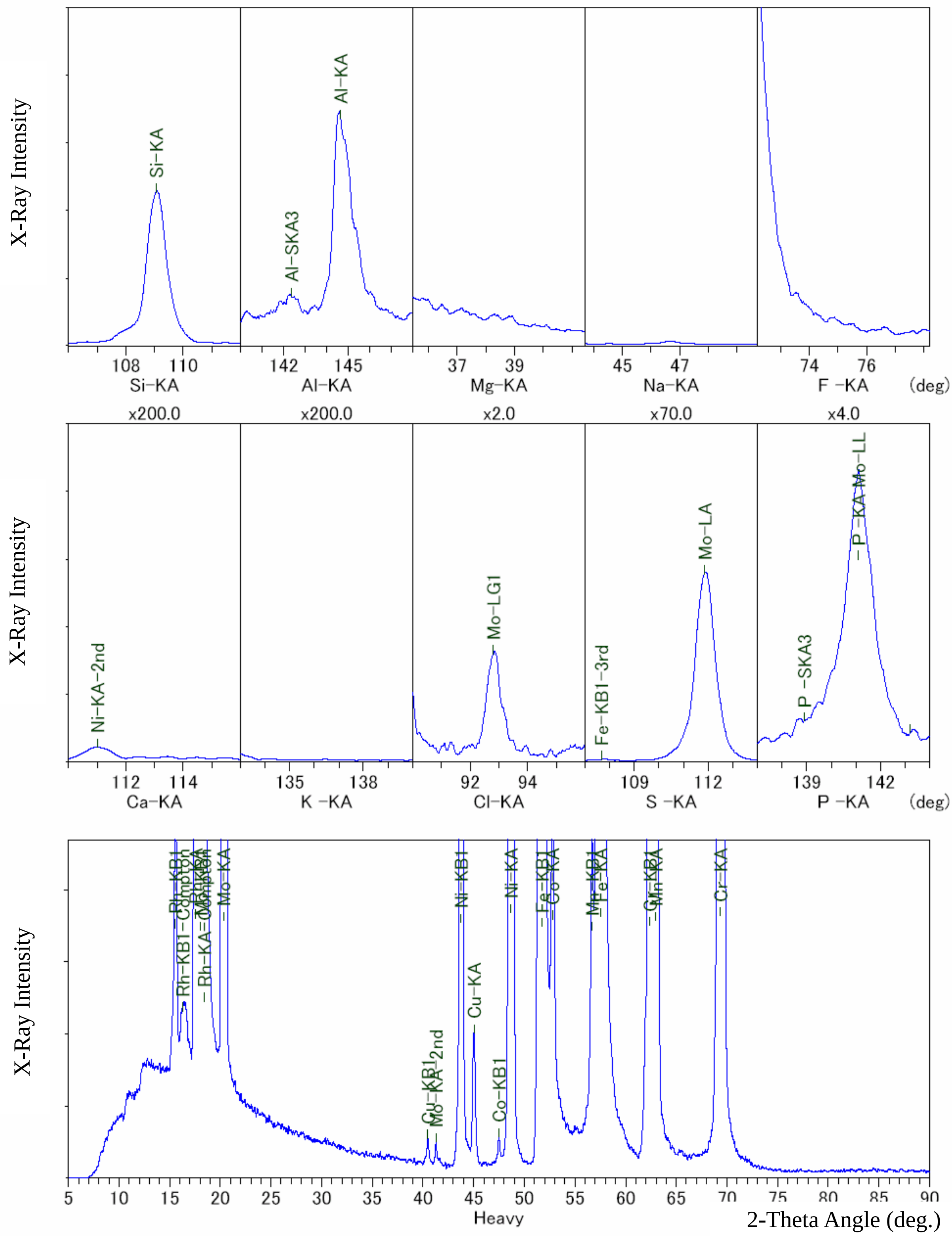


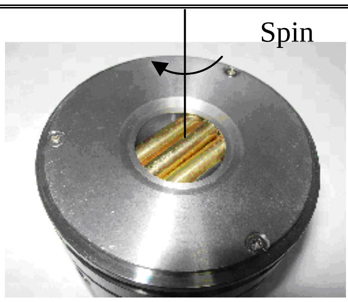
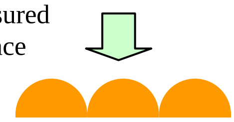
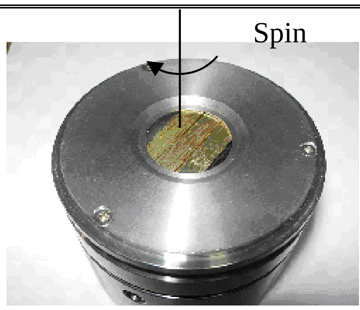
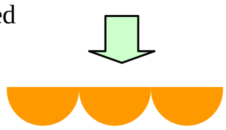
Fig.4 Whole Angle Qualitative Chart of Stainless Steel

3-2 ANALYSIS OF ROUND BARS OF COPPER ALLOY (EXAMPLE OF APPLICATION TO IRREGULARLY SHAPED SAMPLES)

Round bars of copper alloy were analyzed as an example of the analysis of irregularly shaped samples. Three round bars with a diameter of 8mm and a length of 25mm were ground into a semicylindrical shape using a grinder, put in a sample holder and analyzed with a measurement diameter of 20mm. Both convex surface and flat surface were measured and two analysis values were compared. Table 2 shows a result. It is found that the two analysis values are in good agreement. This is because the analysis was made with the shape correction using concentration normalization in spite of the fact that main components were analyzed and the analysis surface was not flat.

Table 2 Analysis Result of Irregularly Shaped Samples

Unit: mass%

Element	Round Bars of Copper Alloy		
	Convex Surface	Flat Surface	Difference
Cu	60.5	60.3	0.2
Pb	2.62	2.67	-0.05
Fe	0.227	0.216	0.011
Sn	0.233	0.230	0.003
Ni	0.046	0.046	0
P	0.025	0.023	0.002
Zn	36.4	36.5	-0.1
Sample Condition	 Measured Surface 	 Measured Surface 	

Fixed angle measurement with 20 sec. for peak and 10 sec. for background

4. CONCLUSION

Since the SQX analysis, which calculates semiquantitative values from the whole angle qualitative analysis, can analyze unknown samples without using standard samples, the SQX analysis can be applied to various fields as shown in Fig.5.

Although this document describes basic examples of applications, the Primus series can be used for the point analysis of a small-diameter sample and the mapping analysis using a built-in CCD camera (option). Since a sensitivity conversion library is standard equipment to analyze small-diameter samples, semiquantitative values can be calculated satisfactorily even for analysis diameters of 10mm, 1mm and 0.5mm. Therefore, the SQX analysis is very useful to analyze samples for research and development from which only small quantities can be taken for analyses and to analyze foreign substances produced in a manufacturing process.[6] Some of those samples are difficult to form in preparation and the loose powder method, which uses high polymer films such as polypropylene and Mylar® to protect the measurement surfaces of samples, may be employed as an analysis method. In that case, fluorescent X-rays in the light element range are absorbed by the high polymer film, but the SQX has the "protection film correction" function and can make semiquantitative calculations by correcting the influence of the attenuation of X-ray intensities.

The SQX has been used for the thickness/composition analysis[7), 8)] for thin film samples by applying the thin film FP method, and has recently been applied to the environmental analysis and to the rapid analysis of toxic metals such as Cd, Pb and Hg, which are attracting attention concerning the WEEE/RoHS Directives and the ELV Directive.[9), 10)]

Fig.5 Application Fields of X-Ray Fluorescence Analysis

Electronic and Magnetic Materials LSIs Memories Magneto-optical disks Magnetic heads LCDs and CRTs Magnet materials	**Chemical Industries** Catalysts Polymers Medicines Fertilizers Pigments and paints Oils, fats and detergents Cosmetics	**Ceramic Industries** Silicon nitride Alumina Glass Firebricks Glazes	**Iron and Steel** Special steel Surface treated steel plate Ferroalloys Cast iron and cast steel Iron ores Plating solutions	**Nonferrous Metals** Aluminum can materials Shape memory alloys Copper alloys Noble metals Nickel alloys Solder
Mining Industries Ores Rocks Volcanic ash	**Oils and Coals** Greases Lubricants Cutting oils Kerosene and heavy oil	**Environment** Effluents Seawater River water Airborne particulate matter Industrial wastes	**Cement and Related Products** Cement Slag Recycle materials	**Others** Soil Rocks Plants Living organisms Foods Cultural properties Nuclear power stations

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