

Analysis of Phosphorus in Resin by EDX - Phosphorus Screening Analysis Kit for TSCA -

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User Benefits

- ◆ The screening analysis package provides everything necessary for analysis including control samples and software.
- ◆ EDX can simultaneously screen for phosphorus, RoHS elements, antimony (Sb) and chlorine (Cl).
- ◆ EDX-7200 can measure phosphorus concentration in resin with high sensitivity.

Introduction

Phenol, isopropylated phosphate (3:1) (PIP (3:1)), is a phosphate compound with three phenyl groups that are isopropylated as shown in Fig 1. It is widely used in resins such as polyvinyl chloride and polyurethane for the purpose of adding plasticity and flame retardancy. Due to directives in the Toxic Substances Control Act (TSCA), the U.S. Environmental Protection Agency (U.S. EPA) has begun regulating the manufacture, processing, and commerce of products and articles containing PIP (3:1).¹

Energy dispersive X-ray fluorescence (EDX) can not perform qualitative or quantitative analysis of organophosphates, but it can analyze the concentration of phosphorus (P) as an element. Therefore, EDX enables screening analysis aimed at controlling total P concentrations in regulated organophosphate compounds. This application news introduces the flow of screening analysis of P using PCEDX-Navi software and examples of screening analysis of P in resins.

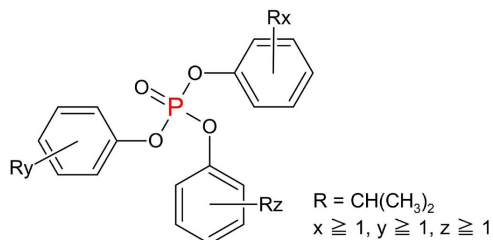


Fig. 1 Structure of PIP (3:1)

P Screening Analysis Kit

Shimadzu has long offered screening analysis kits that support the analysis of RoHS 5 elements (Cd, Pb, Cr, Hg, Br), chlorine (Cl) and antimony (Sb). By using these analysis kits, even novices can screen samples and analyze harmful elements.

As an extension, the EDX-7200 adds a new P screening analysis kit to support screening analysis of organo-phosphate compounds in resins. EDX can, in one sample, simultaneously measure P, RoHS elements, Cl and Sb.

P with the atomic number of 15 has a weaker X-ray fluorescence intensity and hence is more affected by differences in resin materials than elements with larger atomic numbers. In the P screening kit, quantitative values are calculated using the most suitable measurement and calculation conditions that correct for the influence of the resin material.

Screening Setting Display

Fig. 2 shows the threshold settings for the screening analysis kit. From this display, you can set the threshold value for each material and element.

The screening analysis software is also equipped with a time reduction function that automatically shifts to the next measurement condition when it is determined that a managed element clearly exceeds, falls below, or enters a gray zone. The time reduction function therefore significantly increases sample throughput.

		Threshold	Judgment Display	Report Template	
Settings of Threshold(ppm)					
		Material			
		Plastic	Al	Fe	
Element	Cd	<input checked="" type="checkbox"/> 70-130	<input checked="" type="checkbox"/> 70-130	<input checked="" type="checkbox"/> 70-130	
	Pb	<input checked="" type="checkbox"/> 700-1300	<input checked="" type="checkbox"/> 700-1300	<input checked="" type="checkbox"/> 700-1300	
	Cr	<input checked="" type="checkbox"/> 700-1300	<input checked="" type="checkbox"/> 700-1300	<input checked="" type="checkbox"/> 700-1300	
	Hg	<input checked="" type="checkbox"/> 700-1300	<input checked="" type="checkbox"/> 700-1300	<input checked="" type="checkbox"/> 700-1300	
	Br	<input checked="" type="checkbox"/> 300	<input checked="" type="checkbox"/> 300	<input checked="" type="checkbox"/> 300	
	Cl	<input type="checkbox"/> 700-1300			
	Sn	<input type="checkbox"/> 700-1300			
	P	<input checked="" type="checkbox"/> 700-1300			
	Meas. Condition	Precise filter			<input type="checkbox"/> Time Reduction
	Estimated Time	6 minutes	6 minutes	6 minutes	6 minutes

Fig. 2 Setting Display (Example of Threshold Setting)

Management Sample

For equipment management, the P containing polyethylene control sample included in the analysis kit is used. Fig. 3 shows the appearance of the control sample.



Fig. 3 Check Sample of P Screening Analysis Kit

Limit of Detection

Table 1 shows the limit of detection of P in air atmosphere.

Measurement atmosphere	Air
Limit of Detection [ppm]	12

*Measurement time: 100 sec, PE resin sample

Sample

Moldings made of P containing polyvinyl chloride (PVC) resin were analyzed. Fig. 4 shows a photograph of the samples. When measuring, four molded articles were measured side by side.



Fig. 4 Sample appearance

Analysis Results

A total of six elements, RoHS and P, were analyzed using conventional screening analysis conditions. The judgment result is shown in Fig. 5. The quantitative values and the judgement with "OK / ?? / NG" is displayed. The profile of P is also shown in Fig. 6.

P was measured in replicate 10 times. The results are shown in Table 2.

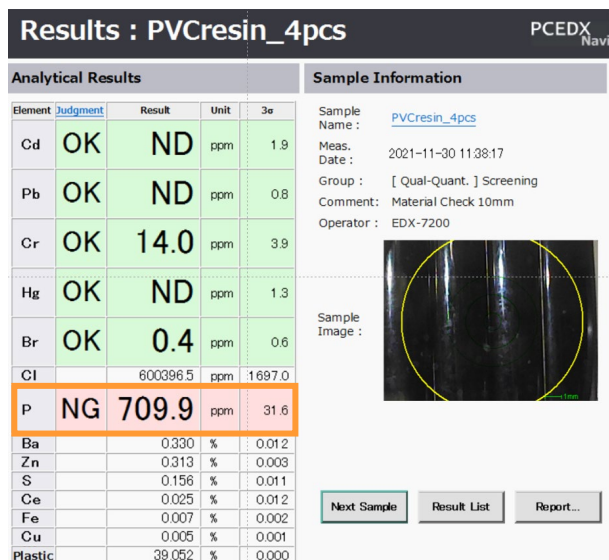


Fig. 5 Screening Analysis and Judgment Results Screen

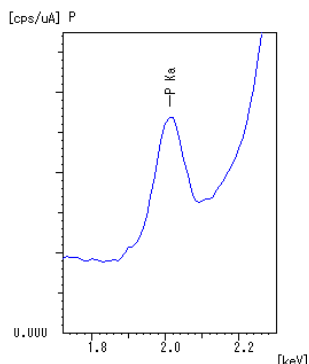


Fig. 6 P Kα Profile

Table 2 Replicate Results

Measurement atmosphere	Air
Mean [ppm]	714.3
Standard deviation [ppm]	13.1
CV value [%]	1.8

Reference: Measurements under Vacuum

Measurements under vacuum atmosphere allow analysis of even lower concentrations of P. Although it is a separate condition from the RoHS screening analysis condition, it is useful for analyzing P more sensitively or for screening only P in resins.

Table 3 shows the limit of detection of P in vacuum atmosphere. Fig. 7 shows a comparison of the P profile intensities under vacuum and air atmosphere. Under vacuum, the detection limit is 4.7 ppm, which is about 2.6 times more sensitive than in air.

Table 3 Limit of Detection

Measurement Atmosphere	Vacuum
Lower Limit of Detection [ppm]	4.7

*Measurement time: 100 sec, PE resin sample

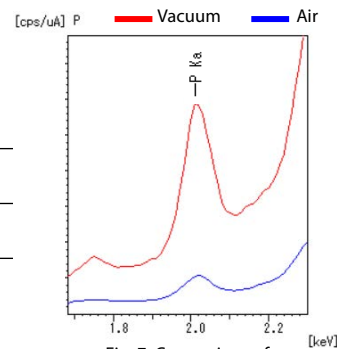


Fig. 7 Comparison of P Kα Profile Intensity

Conclusion

The EDX-7200 P screening analysis kit features:

- Everything necessary for analysis including control samples, and software.
- Screen phosphorus (P) simultaneously with RoHS 5 elements, Cl and Sb.
- Intuitive and easy to use PCEDX-Navi software allowing even those unfamiliar with analysis to easily operate from measurement to judgement to report.

*See "Application News No. 01-00300-EN RoHS Screening Analysis by EDX" for the flow of analysis using the screening analysis kit.

Measurement conditions

Table 4 Quantitative Analysis Conditions

Equipment	: EDX-7200
Element	: ¹⁵ P
Analysis group	: Screening
Detector	: SDD
X-ray tube ball	: Rh target
Tube voltage	: 50 [kV]
Tube current	: Auto [μA]
Collimator	: 10 [mmφ]
Primary filter	: #1
Atmosphere	: Air / Vacuum
Integration time	: 100 sec
Deadtime	: Up to 30 (%)

<References>

- 1) Persistent, Bioaccumulative, and Toxic (PBT) Chemicals under TSCA Section 6(h) URL: <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/persistent-bioaccumulative-and-toxic-pbt-chemicals> (see 2023-3-6)