Rapid analysis of harmful heavy metals in pet food using EDXRF

Hirokazu Moriya[1]
(1) Shimadzu Corporation, Analytical & Measuring Instruments Division, Japan

1. Introduction

- On June 1, 2009, the Act on Ensuring the Safety of Pet Food was enacted in Japan, and compositional standards for dog and cat food were established. The ordinance specifies maximum levels for toxic heavy metals in pet food: cadmium (Cd) ≤ 1 µg/g, lead (Pb) ≤ 3 µg/g, and inorganic arsenic (As) ≤ 2 µg/g.
- Although atomic absorption spectrophotometry (AA) and inductively coupled plasma mass spectrometry (ICP-MS) are commonly used for heavy metal analysis, they require complicated pretreatment such as acid digestion and skilled operators.
- In this study, we focused on X-ray fluorescence analysis, which enables simple and rapid pretreatment, and analyzed five elements: Cd, Pb, As, mercury (Hg), and selenium (Se). This poster presents the usefulness of X-ray fluorescence analysis for toxic heavy metals in pet food and discusses prospects.

2. Methods

An energy-dispersive X-ray fluorescence spectrometer, ALTRACE (EDXRF; Shimadzu Corporation), was used for the analysis (Fig. 1). Table 1 summarizes the analytical conditions.

The main features of EDXRF are as follows:

- Samples can be analyzed directly or with only simple pretreatment, such as grinding.
- Elements from sodium ($_{11}$Na) to uranium ($_{92}$U) can be analyzed.
- Various sample types, including solids, powders, and liquids, can be analyzed.
- Typical measurement times range from a few minutes to several tens of minutes.
- Quantification limit is well below 1 ppm.

Fig. 1 ALTRACE

Table 1 Analytical Conditions

Elements	Cd	Pb	As	Hg	Se
Analysis line	CdKα	PbLβ$_1$	AsKα	HgLα	SeKα
X-ray tube	Rh target				
Tube voltage	65kV	50kV			
Tube current	Automatic control				
Integration time	300sec.	300 sec.			
Dead time	Max. 40%				
Filter	#1	#5			
Detector	SDD Semiconductor Detector				
Atmosphere	Air				
Collimator	18mmφ				
Quantitative Analytical Method	Calibration Curve Method				

*A separate 100-second measurement for internal standard correction.

3. Sample Pretreatment

Samples were placed in sample containers covered with 5 µm-thick polypropylene film and analyzed. Solid samples were ground with a mixer to homogenize the samples. For powdered specimens, simple compression was performed after placing the sample in the container. Fig. 2 shows the sample images.

Fig. 2 Sample Images
(①Purple sweet potato powder)

4. Calibration Curve

ICP standard solutions were diluted to prepare calibration curves (Fig. 3). To correct for matrix and shape effects, scattered X-rays were used for internal standard correction.
Additionally, spectral overlap corrections were applied to the As calibration curve (for Pb interference) and the Pb calibration curve (for Se interference).
The calibration curve concentrations are as follows:
Cd：5, 2.5, 1, 0.5, 0.25, 0 µg/g　　Pb：5, 2.5, 1, 0.5, 0.25, 0 µg/g
As：15, 7.5, 5, 3, 1.5, 0 µg/g　　Hg：15, 6, 3, 1.5, 0 µg/g
Se：20, 10, 0 µg/g

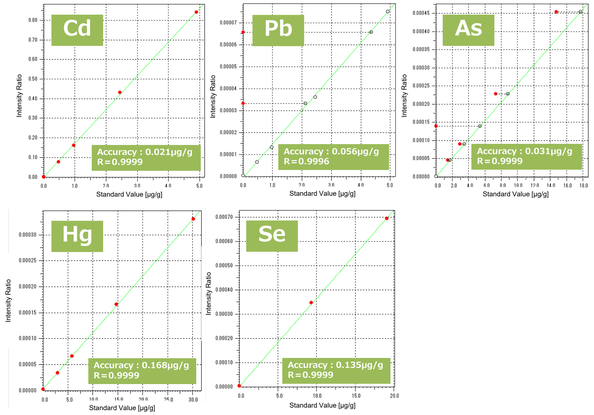

Fig. 3 Calibration Curve

5. Analysis Results

A total of nine samples were analyzed: eight commercially available dog and cat foods and one certified reference material (CRM).
Table 2 shows the quantitative results, and Fig.4 presents the profile overlays.
As and Hg were detected in the cat food samples, possibly due to the use of large fish such as bonito and tuna as major ingredients.

Table 2 Quantitative Results

No.	Sample	Intended Use	Sample Details	Cd	Pb	As	Hg	Se
1	Purple sweet potato powder	For dogs	Freeze-dried, snack	<0.37	<0.24	<0.23	<0.21	<0.08
2	Chicken gizzard		Wet food, snack	<0.33	<0.30	<0.29	<0.23	0.54
3	Complete and balanced food (chicken)		Wet food	<0.26	<0.28	<0.31	<0.36	<0.12
4	Complete and balanced food (chicken)		Wet food	<0.26	<0.32	<0.33	<0.33	<0.12
5	Complete and balanced food (meat + seafood)	For cats	Dry food	<0.35	<0.26	0.35	<0.30	0.59
6	Grilled bonito		Wet food, snack	<0.26	<0.29	2.01	<0.29	1.39
7	Tuna cubes		Dry food, snack	<0.31	<0.44	28.3	1.00	14.8
8	Freeze-dried tuna		Freeze-dried, snack	<0.43	<0.26	3.75	1.62	2.02
9	CRM 7403-a Swordfish meat powder Values in ( ) are standard values	CRM		<0.40 (0.159)	<0.27 (—)	6.16 (6.62)	5.03 (5.34)	2.05 (2.14)

* "<" indicates below the quantification limit. The quantification limit is shown as the theoretical 10σ value.

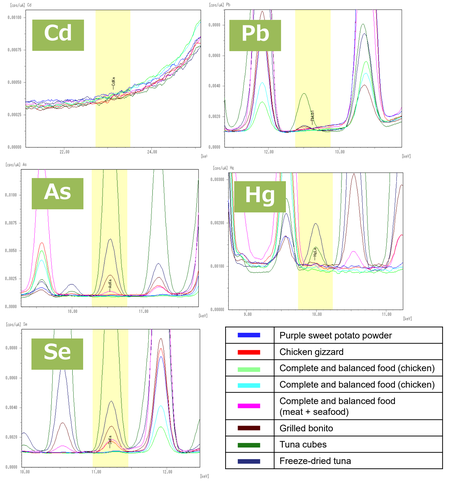

Fig. 4 Profile Overlays

6. Reproducibility

For the freeze-dried tuna sample (No. 8), in which arsenic and mercury were detected, a repeatability test was performed in ten replicates (n = 10).
The results are shown in Table 3.
The relative standard deviation was approximately 1%, indicating good precision.

Table 3 No.8 Freeze-dried tuna: Results of n=10 single repeatability test

	As	Hg	Se
Mean Value [µg/g]	3.721	1.588	1.996
Standard Deviation [µg/g]	0.032	0.025	0.024
RSD [%]	0.86	1.57	1.18

7. Conclusion

X-ray fluorescence analysis enables the determination of harmful heavy metals with simple sample pretreatment. ALTRACE, characterized by its high sensitivity, demonstrated a lower limit of quantification sufficient for analysis at the level of a few ppm, as well as good reproducibility.
Since XRF is an elemental analysis technique, separate analysis is required to distinguish between the chemical forms of inorganic and organic arsenic; however, it is considered useful for the screening of hazardous heavy metals.