

## Chemical Analysis Research Center

The Chemical Analysis Research Center has been developing new methods of analyzing environmental chemicals and has been studying the fate of these compounds in plants, water, and soils.

The **Environmental Chemicals Analysis Laboratory** has been studying the fate of organoarsenics such as diphenylarsinic and phenylarsonic acids in paddy fields. By using an LA-ICP-MS (laser ablation inductively coupled plasma mass spectrometry) system we have developed a new method for analyzing cadmium (Cd) concentrations in grains such as rice, wheat, and soybean. We are able to measure the Cd concentration in grains without the need for pretreatment, and we have clarified the distribution of Cd in rice grains. Furthermore, our laboratory has developed a convenient method of clean-up samples for dioxin analysis. Gel permeation chromatography is the most effective way to remove the waxes from plant samples destined for dioxin analysis (Topic 1). Laboratory members are also studying the use of ELISA (enzyme-linked immunosorbent assay) for the detection of pesticide residues in crops. In September 2004 we ran a training course on "How to measure pesticide residues in crops by ELISA".

The **Radioisotope Analysis Laboratory** has been surveying the fallout of artificial radioisotopes such as  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in wheat, rice, and soils collected from all over Japan since 1957. These data have been used to determine the fate of these radioisotopes in the soil. Laboratory members are also studying prediction of the fate of  $^{129}\text{I}$  discharged from nuclear fuel processing plants, and they have constructed a system for the large-scale extraction of iodides from soil and plants. The results suggest that 0.1 Bq  $^{129}\text{I}$  / kg soil may be detected. To clarify the fate of iodides in paddy fields, we have been using the XANES (X-ray absorption near edge structure) method to investigate changes in the chemical form of iodides in the soil (Topic 2).

Yellow sand frequently blows across to northern Japan in the early spring. Because the fallout of artificial radioisotopes such as  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  has also been increasing in these areas, we have begun a study to determine the source of the yellow sand.

Dr. Noriko Yamaguchi, researcher at the Radioisotope Analysis Laboratory, was awarded a progress award by the Japanese Society of Soil Science and Plant Nutrition.

### Topic 1: Clean-up of species interfering with dioxin analysis in leafy vegetables

In general, the analysis of PCDD/Fs and PCBs requires labor-intensive, multi-step clean-up procedures that are both expensive and time consuming. Therefore, a rapid and reliable analytical method is needed. Recently, we reported on the efficiencies of PCDD/Fs analyses based on a variety of extraction techniques such as supercritical fluid extraction (SFE), accelerated solvent extraction (ASE), and automated soxhlet techniques. In Japan, dioxin analysis in foods is essentially performed according to the "Provisional guidelines for methods of analysis of dioxins and Co-PCBs in food" (Ministry of Health, Japan, 1999). However, because vegetables contain various interfering species, such as oils, pigments, or waxes, an additional clean-up procedure is required high clean-up efficiencies for the dioxins analysis. To remove interfering species (long-chain aliphatic compounds) from leafy vegetables, we tested the application of conveniently available clean-up procedures, using a homemade multi-layer silica gel column combined with a Carboxen 1016 (75 mg) short column (Fig. 1). Figure 2 shows the interfering species in the mono-*ortho* PCB fraction after a typical column chromatography clean-up of leafy vegetable samples on the basis of the present Japanese dioxin analysis method. The results obtained by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and GC-MS indicated that these species were mainly hentriacontane ( $\text{C}_{31}\text{H}_{64}$ ), accompanying nonacosane ( $\text{C}_{29}\text{H}_{60}$ ), components of the pathway for synthesis of the principal components of wax. Elution with hexane revealed that the major fractionation of mono-*ortho* PCBs occurred in the 30 to 80 mL hexane eluate. Thus (Fig. 3), the 0 to 30 mL hexane elution step

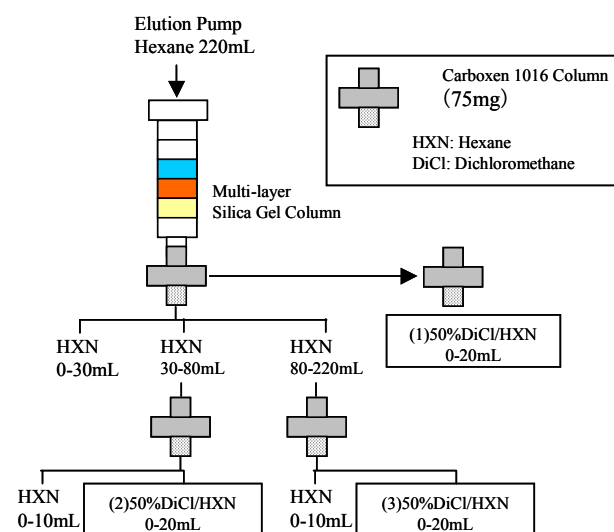


Fig. 1 Procedure used for clean-up of a mono-*ortho* PCBs fraction.

allowed us to remove hentriacontane and nonacosane from spinach samples. The interfering species (alkanes) were found mainly in the hexane eluate. We confirmed that hentriacontane and nonacosane could be removed by washing with hexane using a Carboxen 1016 short column.

Thus, almost nothing of the interfering species (alkanes) remained in the 50-vol% dichloromethane/hexane elution (Fig. 1 (1), (2), (3)). The sum of the recovery percentages of mono-*ortho*-Co-PCBs in the spinach samples was over 80% (Fig. 4). We concluded that the proposed method of using a Carboxen 1016 short column is effective on removing long-chain alkanes from leafy vegetables. (H. Eun)

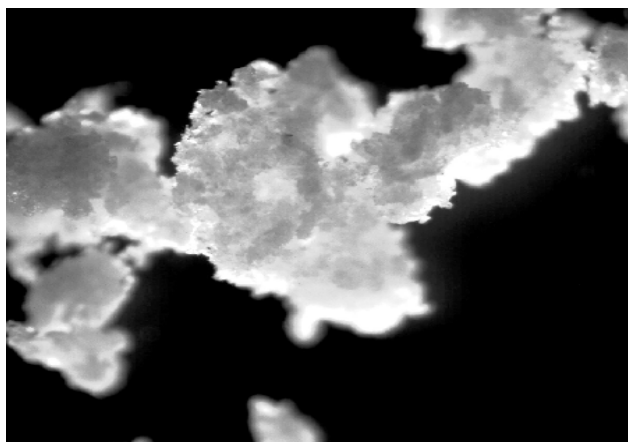


Fig. 2 Crystals of interfering compounds obtained during the clean-up procedure.

## Topic 2: Cause of eluviation of iodine in flooded paddy fields

Because of its very long half-life (16 million years), iodine-129 is one of the most hazardous gaseous radionuclides leaked from nuclear fuel reprocessing plants. For the sake of food safety and security, it is critical that the behavior of  $^{129}\text{I}$  in agricultural environments be investigated. A previous study in our laboratory revealed that iodine concentrations in paddy field soils were substantially lower than in upland fields and forest soils. The drop in redox potential during the period when the paddy soils are flooded may cause the reduction of  $\text{IO}_3^-$  to  $\text{I}^-$ , and, as a result, the solubility of iodine may increase. By applying nondestructive analysis using XANES (proposal no. 2004B0093-NXa-np), we investigated whether changes in the state of oxidation of iodine species occur

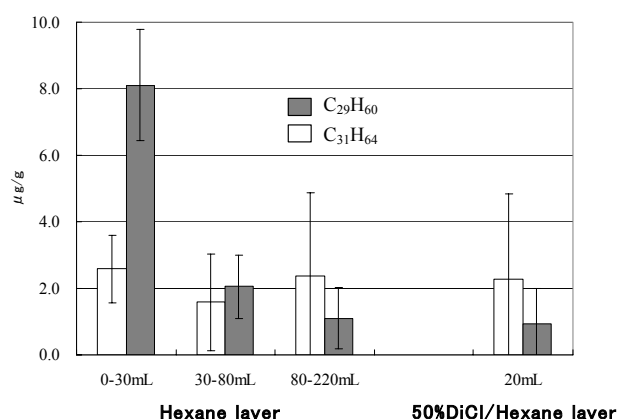


Fig. 3 Concentrations of hentriacontane ( $\text{C}_{31}\text{H}_{64}$ ) and nonacosane ( $\text{C}_{29}\text{H}_{60}$ ) in each fraction.

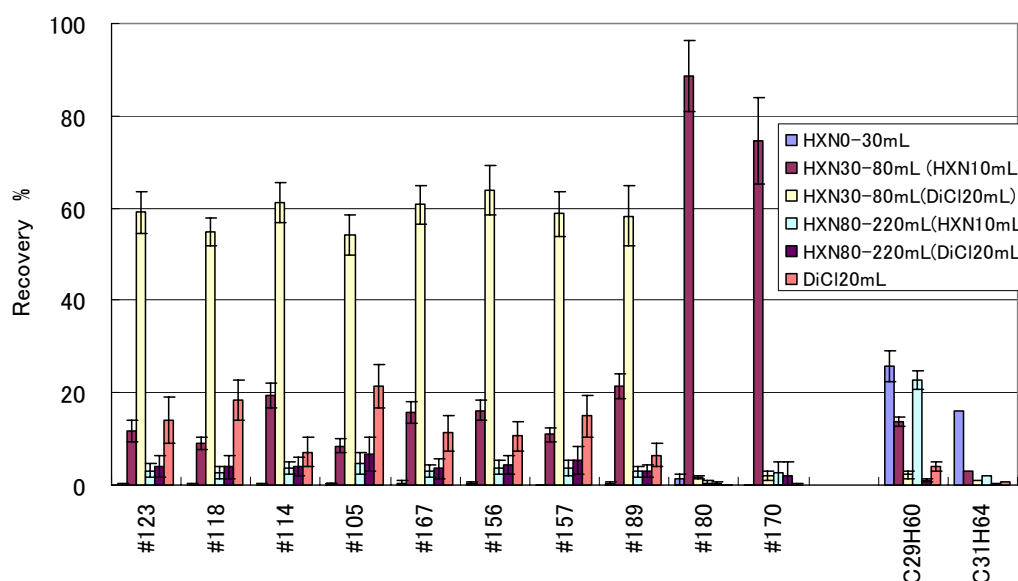


Fig. 4 Percentage recovery of mono-*ortho* PCBs in each fraction from spinach samples.

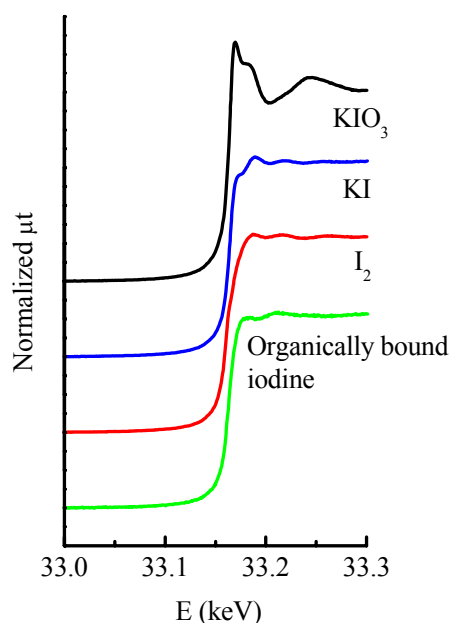


Fig. 5 XANES spectra of iodine reference materials.

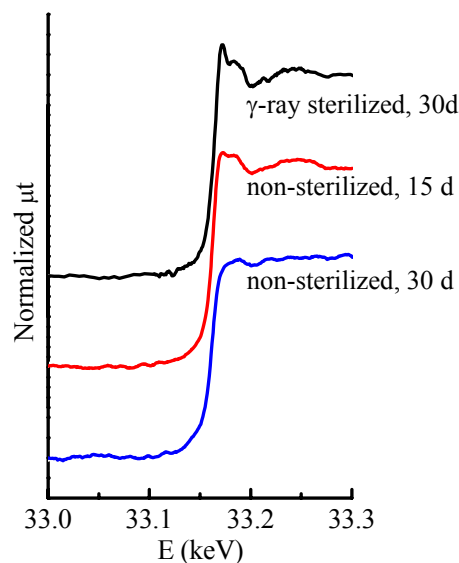


Fig. 6 XANES spectra of iodine on paddy soil after incubation under flooded conditions.

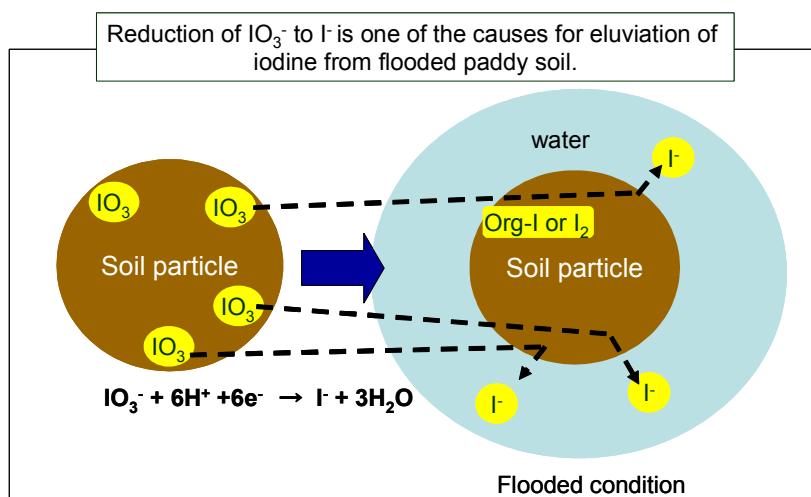


Fig. 7 Mechanism of iodine eluviation in a flooded paddy soil.

in flooded soil systems and thereby affect the species' mobility in the soil environment.

Figure 5 shows the reference XANES spectra of  $\text{KIO}_3$ ,  $\text{KI}$ ,  $\text{I}_2$ , and organically bound iodine. Iodate ( $\text{IO}_3^-$ ) had a very obvious post-edge structure, whereas those of  $\text{KI}$ ,  $\text{I}_2$ , and organically bound iodine were weak. The XANES post-edge feature distinctively indicated the presence of  $\text{IO}_3^-$  in the sample. Figure 6 shows the XANES spectra of iodine that was spiked into paddy soils as  $\text{IO}_3^-$ , after which the soils were incubated for 15 or 30 days. Disappearance of the XANES post-edge feature of  $\text{IO}_3^-$  showed that the decreased concentration of iodine in the paddy soil was the result of a reductive reaction of  $\text{IO}_3^-$  when the paddy field was under anaerobic

conditions. The reduced products would be  $\text{I}^-$  and  $\text{I}_2$  or organically bound iodine. The concentration of  $\text{I}^-$  in solution phase increased after incubation under flooded conditions. Therefore, the  $\text{I}^-$  formed was not retained by the soil but was dissolved into the solution phase, whereas  $\text{I}_2$  or organically bound iodine remained in the solid phase of the soil. Sterilization of the paddy soils inhibited the reduction of  $\text{IO}_3^-$  (Fig. 6). In conclusion, biological consumption of oxygen in the soil and the subsequent drop in redox potential are important to the reduction reaction of  $\text{IO}_3^-$  and cause eluviation of iodine as  $\text{I}^-$  in paddy soil systems (Fig. 7). (N. Yamaguchi)