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Application News

No. A641

Spectrophotometric Analysis

# Analysis of Resin-Coated Fertilizers by FTIR: Analysis Conforming to "Identification Methods for Fertilizers (2020)"

In Japan, official specifications and application standards for fertilizers are established in the Fertilizer Regulation Act [1] in order "to preserve the quality, etc. of fertilizers and to ensure fair trade in fertilizers and their safe application." Analysis methods for fertilizers, which are important for preserving fertilizer quality, are provided in "Testing Methods for Fertilizers (2020)" and "Identification Methods for Fertilizers (2020)." "Identification Methods for Fertilizers" states that "unlike analysis methods for measuring the components, etc. in fertilizers, identification methods are used in observation of the morphology and estimation of the raw materials used" [2] and describes identification by microscopic observation, detection of fertilizer components by reagents and litmus paper, and identification by X-ray diffraction instruments, among other methods. Identification by Fourier transform infrared spectrophotometry (FTIR) was newly added to "Identification Methods for Fertilizers (2020)." Qualitative analysis by measurement of the infrared spectrum by FTIR can be completed in a short time without complex sample preparation.

Application News No. A638 introduced an identification test of a urea-isobutyl aldehyde condensate compound fertilizer, which is known as chemical slow-release fertilizer. In this article, an analysis of the coating materials and fertilizer cores of resin-coated fertilizers was carried out, and their raw materials were identified.

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## Fertilizer Identification Conforming to "Identification Methods for Fertilizers (2020)"

Table 1 shows the outline and an example of the measurement conditions for identification by the FTIR method provided in "Identification Methods for Fertilizers (2020)."

**Table 1 Identification Method for Fertilizers by FTIR**

| | |
|---|---|
| Outline | Applicable to fertilizers in which organic compounds are used as raw materials and to resin-based coating materials of coated fertilizers. |
| Measurement conditions | |
| Measurement method | Total reflection spectroscopy (attenuated total reflection: ATR) |
| Wavenumber range | 4000 $cm^{-1}$ - 650 $cm^{-1}$ |
| Resolution | 4.0 $cm^{-1}$ |
| Accumulation time | 30 sec - 60 sec (approx.) |
| Identification methods | ①Comparison with infrared absorption spectrum of a known compound<br>②Search using infrared absorption database |

The target fertilizers for identification by FTIR include fertilizers in which the raw material is an organic compound, such as ureide compounds, and raw materials of resin-based coating materials for coated fertilizers.

The attenuated total reflection spectroscopy (ATR spectroscopy), which is mentioned as the measurement method, is a technique in which the measurement is carried out by placing the sample in close contact with a prism made of an infrared-transmitting material. This is an extremely simple technique, as almost no sample preparation is required. The prism can be selected according to the sample material and the purpose of the analysis, and a diamond prism, ZnSe, and other material can be used as prisms for measurements to 650 $cm^{-1}$. Details concerning the principle of the ATR spectroscopy and the influence of the type of prism on the data may be found in Application News No. A485.

The identification methods are broadly divided into two techniques, as follows. In ① "Comparison with the infrared absorption spectrum of a known compound," the general method is to check whether a designated peak is specified or not, and if not specified, to visually check whether the total peak shapes are identical or not. In cases where a standard sample is measured for comparison with the spectrum of the test sample, it is possible to use a similarity calculation, utilizing a function of the software. In ② "Search using infrared absorption database," the search methods include searches using a commercially-available library and searches in which the spectra of standard samples are measured in advance and recorded in the user's original private library. In this experiment, identification was conducted by ② "Search using infrared absorption database."

## Coated Fertilizers

Coated fertilizers are fertilizers in which elution of the fertilizer components can be controlled by coating the surface of the fertilizer particles with a coating that delays penetration of water [3]. Acetaldehyde-condensed urea and urea-isobutyl aldehyde condensate, which are known as slow-release fertilizers, are termed controlled release fertilizers by chemical modification, while coated fertilizers are termed controlled release fertilizers by physical modification. Because the duration and speed of elution of coated fertilizers are controlled by changing the coating film thickness and material, these fertilizers have the distinctive features of high controllability of fertilizer elution and sustainability of the fertilizer effect [3]. The materials used in coatings include sulfur, polyolefin resin, alkyd resin, and others. As mentioned previously, among these substances, the object of identification by FTIR in the "Identification Methods for Fertilizers (2020)" is resin-based coatings. "Identification Methods" states that "In the case of coated fertilizers, solids except the fertilizer components may be used as the test sample," and describes a spectrum measured by "pulverizing the sample, adding water and stirring with a stirrer, and natural drying" as an example of measurement [2].

## Measurement System

The measurement system used in this experiment comprised the IRSpirit™ Fourier transform infrared spectrophotometer with the QATR™-S single-reflection ATR accessory which perfectly fits in the sample compartment. Fig. 1 shows the external appearance of the system. A diamond prism was used.

**Fig. 1 External Appearance of IRSpirit™ + QATR™-S**

## Analysis of Resin-Coated Fertilizers

Three commercial coated fertilizers (A to C) were analyzed based on "Identification Methods for Fertilizers (2020)." Fig. 2 shows the appearance of the fertilizers used in the analysis, where the upper row shows the coated fertilizers and the lower row shows the sampled coating fragments. The coating fragments were obtained by lightly crushing fertilizer granules with a diameter of approximately 3 to 4 mm as a pretreatment, sampling some of the fragments, and washing the fragments with pure water, followed by natural drying.

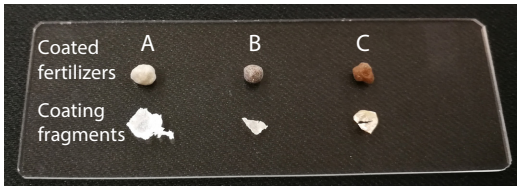


**Fig. 2 External Appearance of Coated Fertilizers (Top) and Coating Fragments (Bottom)**

The coating fragments and the internal fertilizer cores of coated fertilizers A to C were measured by the ATR spectroscopy. Table 2 shows the measurement conditions, Fig. 3 shows the spectra of the coating fragments, and Fig. 4 shows the spectra of the fertilizer cores.

**Table 2 Measurement Conditions**

| | |
|---|---|
| Instrument | : IRSpirit-T (KRS-5 window)<br>QATR-S (wide-band diamond disk) |
| Resolution | : 4 $cm^{-1}$ |
| Accumulation | : 45 times |
| Apodization function | : Sqr Triangle |
| Detector | : DLATGS |

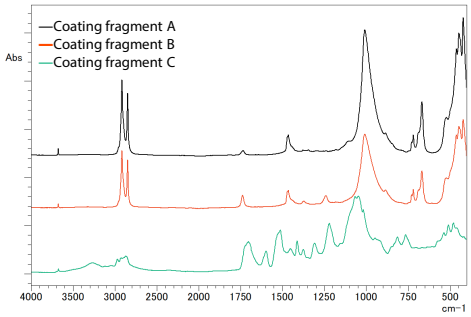


**Fig. 3 ATR Spectrum of Coating Fragments**

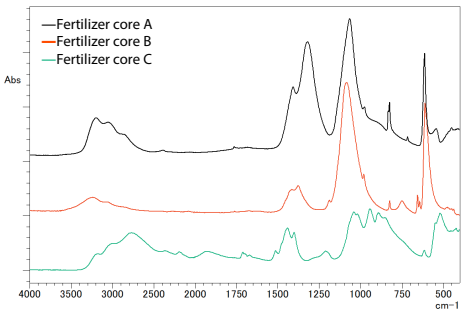


**Fig. 4 ATR Spectra of Fertilizer Cores**

A library search of the respective spectra was carried out, and a qualitative analysis of the materials was conducted. Table 3 shows the results.

Coating fragment A was identified as polyethylene (PE) containing magnesium silicate (talc), fragment B was identified as ethylene-vinyl acetate (EVA), also containing talc, and fragment C was identified as polyurethane. The qualitative analysis of these coating materials was carried out referring to the library provided in LabSolutions™ IR as a standard feature, a Shimadzu FTIR control software. As one example, Fig. 5 shows the overlay of the spectrum of coating fragment A and the library spectra. The peaks of the sample spectrum are in good agreement with those of the spectrum of PE, and peaks originating from talc were confirmed around 1000 $cm^{-1}$ and 3700 $cm^{-1}$.

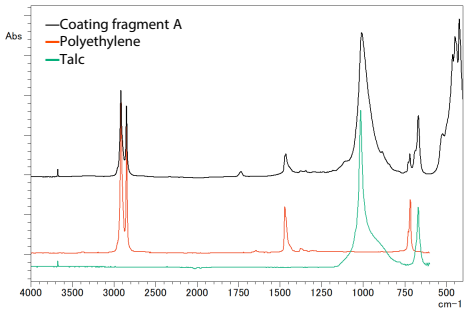


**Fig. 5 Overlay of Spectrum of Coating Fragment A and Library Spectra**

Although the fertilizer core of coated fertilizers is not an object of analysis by FTIR, the type of inorganic salt can be estimated from the infrared spectrum. A search of the fertilizer cores was conducted using the Wiley software KnowItAll and spectrum database. As shown in Table 3, fertilizer core A is estimated to be a mixture of ammonium sulfate and nitrate, B is estimated to be a mixture of sulfate and ammonium salt, and C is estimated to be ammonium phosphate. (The search results for the fertilizer cores are omitted here.) In all cases, these are generally used as chemical fertilizers and are objects of identification by X-ray diffraction instruments in "Identification Methods for Fertilizers (2020)." Therefore use of an X-ray diffraction instrument is recommended when identification of the fertilizer cores is necessary.

**Table 3 Qualitative Analysis Results of Coated Fertilizers A - C**

| Coated fertilizer | Coating fragment | Fertilizer core |
|---|---|---|
| A | PE + talc | Ammonium sulfate + nitrate |
| B | EVA + talc | Sulfate + ammonium salt |
| C | Polyurethane | Ammonium phosphate |

## Conclusion

The raw materials of the coating materials of resin-coated fertilizers were identified by an analysis method conforming to "Identification Methods for Fertilizers (2020)." It was found that the three types of coating fragments measured here were all coatings consisting of different materials.

<References>

(1) Food and Agricultural Materials Inspection Center (FAMIC), "Fertilizer Regulation Act" http://www.famic.go.jp/ffis/fert/hourei/sub1_torihou.htm (accessed July 17, 2020, Japanese)
(2) Food and Agricultural Materials Inspection Center (FAMIC), "Identification Methods for Fertilizers" http://www.famic.go.jp/ffis/fert/obj/kanteiho_2020.pdf (accessed July 17, 2020, Japanese)
(3) Ministry of Agriculture, Forestry and Fisheries, "Use Technologies for Slow-Release Fertilizers" (Controlled Release Fertilizers) https://www.maff.go.jp/j/seisan/kankyo/hozen_type/h_sehi_kizyun/pdf/ntuti30.pdf (accessed July 31, 2020, Japanese)



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