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Application News

No. A638

Spectrophotometric Analysis

Identification Test of Fertilizer 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 of fertilizers, etc. and ensure fair trade in fertilizers and their safe application." Analysis methods for fertilizer, 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]. Applicable identification methods include identification by microscopic observation, detection of fertilizer components by reagents and litmus paper, and identification by X-ray diffraction instruments. In "Identification Methods for Fertilizers (2020)," identification by Fourier transform infrared spectrophotometry (FTIR) was newly added to the applicable methods. Measurement of the infrared spectrum by FTIR can be completed in a short time and does not require complex sample preparation.

In this article, measurement of the infrared spectrum and identification testing of a urea-isobutyl aldehyde condensate compound fertilizer were carried out.

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

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

Table 1 Identification Method for Fertilizers by FTIR

Outline	Applicable to fertilizers using organic compounds 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	① Comparison with infrared absorption spectrum of a known compound ② Search using infrared absorption database

The target fertilizers for identification by FTIR include fertilizers in which organic compounds such as ureide compounds are used as the raw materials and resin-based coating materials for coated fertilizers.

In the attenuated total reflection spectroscopy (ATR spectroscopy) mentioned as the measurement method, the measurement is carried out with the sample placed 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. A diamond prism, ZnSe, and other types can be used as prisms for measurements to 650 cm^{-1}. For details concerning the principle of the ATR spectroscopy and the influence of the type of prism on the data, please refer to Application News No. A485.

The identification methods are broadly divided into two techniques, as follows. In ① "Comparison with 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 spectrum shapes are identical or not. In cases where a standard sample is measured for comparison with the spectrum of the test sample, a similarity calculation using the "Purity Calculation" function of the IR Pilot software is possible. In ② "Search using infrared absorption database," various methods are possible, including searches using a commercially-available library and searches in which the spectra of standard samples are measured in advance and recorded in a private library. In this experiment, we used ① "Comparison with infrared absorption spectrum of a known compound."

Measurement System

The measurement system used here comprised the IRSpirit™ Fourier transform infrared spectrophotometer with the QATR™-S single-reflection ATR accessory which perfectly fits in the sample compartment of the IRSpirit. Fig. 1 shows the external appearance of the system. A diamond prism was used. The dedicated IR Pilot™ program provided as a standard feature of the IRSpirit includes a program for identification tests which enables simple identification testing, even by inexperienced personnel, based on detection of the specified peak of the spectrum and the degree of similarity of the spectrum shape.

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

Urea-Isobutyl Aldehyde Condensate Compound Fertilizer

Urea-isobutyl aldehyde condensate, also called isobutylidene diurea (IBDU), is a single compound which is produced by condensation of urea and isobutyl aldehyde. Because IBDU is sparingly soluble in water and is gradually mineralized by hydrolysis and microbial degradation, it is well known as a chemical slow-release fertilizer that demonstrates its effect as a fertilizer over an extended time.

In this experiment, we analyzed a compound fertilizer containing urea-isobutyl aldehyde condensate. Fig. 2 shows the appearance of the fertilizer used in the analysis.

Fig. 2 Urea-Isobutyl Aldehyde Condensate Compound Fertilizer

Granular fertilizer with a diameter of approximately 8 to 10 mm was crushed lightly, and part of the fertilizer was taken as a sample and measured while pressed on the ATR prism. Table 2 shows the measurement conditions, and Fig. 3 shows the measured spectrum. An identification test was then carried out using this spectrum as the spectrum of the standard sample.

Table 2 Measurement Conditions

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

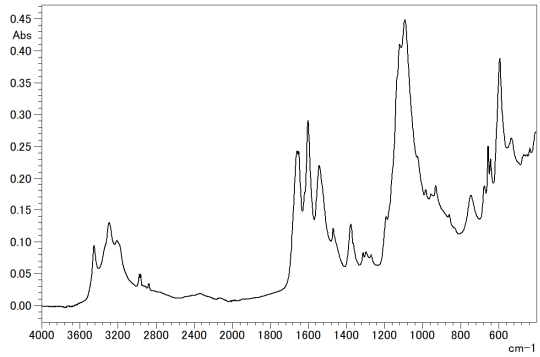

Fig. 3 ATR Spectrum of Urea-Isobutyl Aldehyde Condensate Compound Fertilizer

Identification Test Using IR Pilot

The IR Pilot dedicated program of IRSpirit was used in the measurement of the test sample spectrum and preparation of the identification test report. IR Pilot has convenient functions that enable easy operation in all processes from measurement and analysis of the target sample to printout of the report simply by selected four items in accordance with the instructions on the screen. The four items, as shown in the workflow of measurement using IR Pilot in Fig 4, are ① Selection of analysis purpose, ② Selection of measurement technique, ③ Selection of type of ATR prism, (not required when using the accessories with automatic recognition) and ④ Data processing. When the purpose of the analysis is selected from (a) Main Menu, measurement by the dedicated program begins. Here, if "Identification Test" is selected, a dialogue box (b) appears, asking "Does this measurement correspond to a pharmacopeia?" If the answer is "Yes," resolution is set automatically to 2 cm^{-1}, and if "No," resolution is set to 4 cm^{-1}. In this experiment, we selected "No." The next step is selection of the measurement technique. At this time, the measurement wavenumber range is set automatically corresponding to the measurement technique. Because accessories are recognized automatically when using the QATR-S, only the type of prism to be used is selected from screen (c). All measurement conditions shown in Table 1 can be selected by this operation. BKG measurements, sample measurements, and data processing are also navigated by the program. In case "Purity Calculation" is to be used, "Purity" is selected from screen (d) Data Processing Options after completion of the spectrum measurement, and the spectrum of the standard sample, which has been measured in advance, is selected from screen (e) Parameters for Purity Calculation. Fig. 5 shows the results of the identification test. An overlay of the spectra of the standard sample and the test sample and the calculated purity score (upper right in the figure) are printed out as a report. Here, the spectra shapes were in good agreement, and the purity score was calculated as 0.9937. Because the test sample absorbed the same intensities at the same wavenumbers as in the spectrum of standard sample, identity with the standard sample was confirmed.

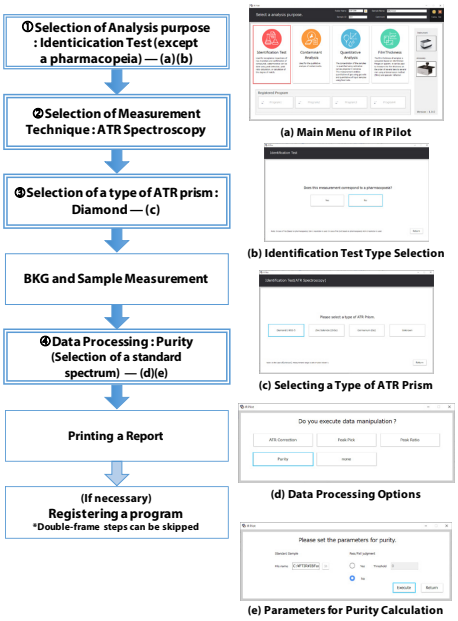

Fig. 4 Workflow of Identification Test Using IR Pilot

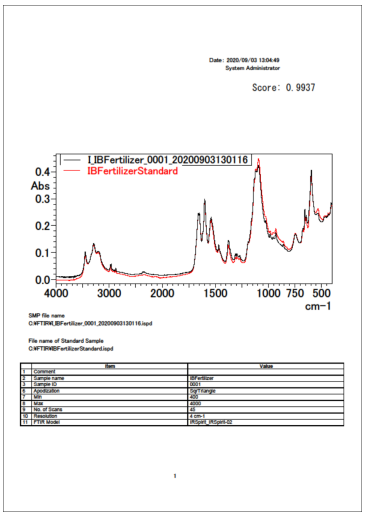

Fig. 5 Example of Identification Test Report Printout

Conclusion

An identification test conforming to "Identification Methods for Fertilizers (2020)" was conducted using a urea-isobutyl aldehyde condensate compound fertilizer, which is known as a slow-release fertilizer. Automation of test condition setting and the actual measurement is possible by using the IR Pilot dedicated program of Shimadzu's IRSpirit, enabling simpler and more reliable identification testing.

<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)

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