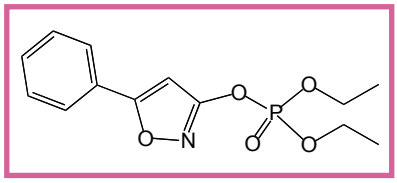
Application of qNMR: Quality control of organophosphorus pesticides

Quantitative NMR (qNMR) is widely applicable for determining purity, since the method does not require a target compound of known purity as a reference.

This Note introduces an application of qNMR to quality control, where purity of commercial organophosphorus pesticides (isoxathion oxon) is determined.

< Target compound: Isoxathion oxon >

Two standard samples for pesticide residue test, isoxathion oxon, were examined. Information of the products is listed in Table 1.



Isoxathion oxon

Table 1. Compound information attached to the products

Sample	Lot	Purity (%)*	Appearance	m.p. (℃)
starndard isoxathion oxon	1	96.9	Yellow-brown crystalline powder	49.5
	2	98.9	White crystalline powder	51.7

* Determined via GC analysis

< qNMR reference >

Hexamethyldisilane (HMD) was used as a qNMR reference. HMD gives an NMR signal at 0 ppm but is not SI-traceable, and so its concentration was calibrated with a certified reference material, diethyl phthalate. Thus, SI-treaceability of qNMR measurements using HMD is established.

< qNMR measurement conditions >

Table 2 shows NMR measurement conditions. Important point is setting a recycle delay to be more than five times of longitudinal relaxation time (T_1), preventing from saturation.

For the details of quantitative analysis using NMR, please refer to technical information of JEOL homepage.

Table 2. Measurement conditions

Parameter of JNM-ECA600	
Observed nucleus	^{1}H
Observed range	-5 to 15 ppm
Data points	32K
Digital filter	On (8 times)
Recycle delay	60 s
Flip angle	90°
Scans	8 scan
Temperature	25℃
Spinning	Off

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<Results and discussion>

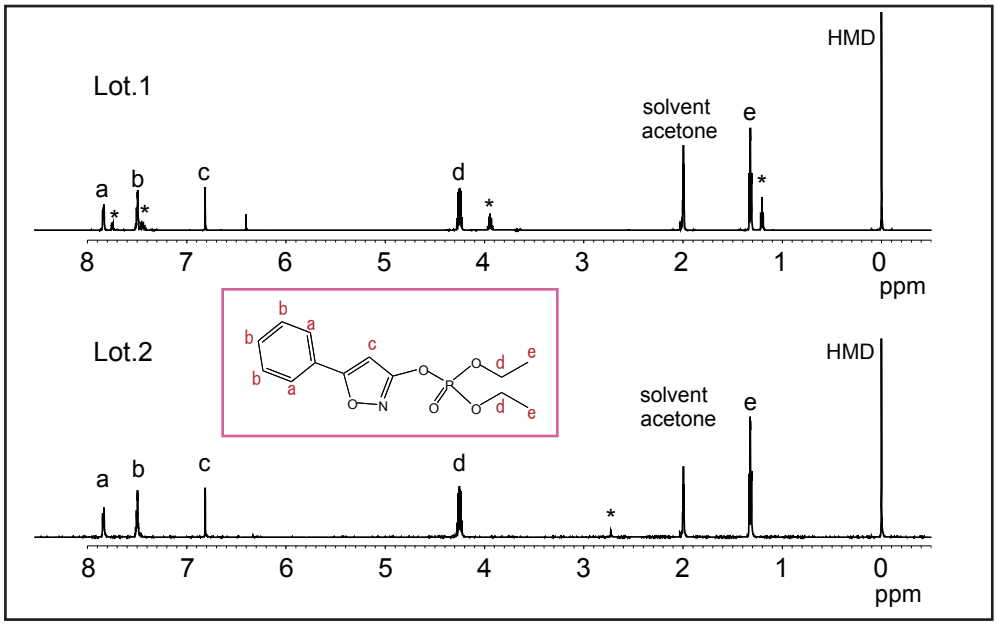

Fig. 1 qNMR spectra of two isoxathion oxon samples

Figure 1 shows NMR spectra of isoxathion oxon Lot.1 and Lot.2. The former spectrum exhibits many impurity peaks (*), suggesting low grade of the product. The concentration deduced from qNMR analysis is listed in Table 3. The result for Lot.2, 98.5±1.3 %, agrees with that in the attached information, while 75.4±0.2 % for Lot.1 is different from 96.9 % in the attached information which is, therefore, considered to be inappropriate. These results are consistent with the concentration ratio determined by GC/MS, although GC/MS has uncertainty due to response factors. Thus, qNMR is promising in wide research fields including quality control.

Table 3. Results of quantification analysis of qNMR and GC/MS

	NMR peak (ppm)					Average	GC/MS
	a	b	c	d	e		Area ratio
	7.85	7.49	6.81	4.25	1.32		
Lot. 1	75.3% (0.8) a)	75.1% (0.9) a)	75.5% (0.7) a)	75.8% (0.9) a)	75.4% (0.9) a)	75.4% (0.2) a)	75.3% b)
Lot. 2	99.0% (0.3) a)	99.3% (0.5) a)	96.3% (0.2) a)	99.4% (0.6) a)	98.6% (1.1) a)	98.5% (1.3) a)	98.5% b)

a) Values in ( ) indicate standard deviation. b) Value for Lot.2 is assumed to be the same as that from NMR, and value for Lot.1 is calculated using concentration ratio.

Ref : M. Tahara, N. Sugimoto,T. Suematsu et. al, *Jpn.J.Food Chem.Safety*, **2009**, Vol.16(1), 28-33

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