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Water Content Using Karl-Fisher Aquametry and Loss on Drying Determinations Using Thermogravimeter for Pesticide Standard Materials

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In the Japanese Food Sanitation Law, the water content or loss on drying (LOD) value of standard materials for pesticide residue analysis is not officially designated. In the present study, to investigate the actual situation of the water content or LOD value of commercial pesticide standards, 40 pesticide standards were determined by the Karl-Fisher aquametry (KF) and 24 pesticide standards were done by a thermogravimetric analysis (TGA). Furthermore, the applicability of KF and TGA was also discussed. The water content or LOD values of most pesticides were within 1%, therefore they are regarded as having the negligible values within the limit of error for the residual pesticide analysis. However, since some pesticides, dichloropropionic acid sodium salt, sodium dimethyl dithiocarbamate, paraquat, diquat dibromide, formamidine hydrochloride, maneb, iminoctadine triacetate, mancozeb and monocrotophos, had relatively large amounts of water or LOD values, the water content and LOD value of such pesticides should be carefully considered during the pesticide residue analysis. For comparison of KF and TGA, there are differences in both the data for some pesticide standards. The reason seems that the pesticides interfere with the KF redox reaction.

Key words —— pesticide standard, thermogravimetry, Karl-Fisher aquametry, water content, loss on drying

INTRODUCTION

In view of analytical science, weighing is very important as an initial step of an analysis. For the purity test of the Japanese Pharmacopoeia XIV, to obtain an accurate weight of a sample requires a value of loss on drying (LOD) or water content value.[1)] Since the purities in dry weight of most drugs are regulated within 100.0 ± 2.0%, the amount of volatile impurity, including water and organic solvent, cannot be ignore. Therefore, LOD, thermogravimetry (TGA) or Karl Fischer aquametry (KF) were mentioned as a general test of the Japanese Pharmacopoeia XIV.[1)] However, the LOD or water content of a pesticide standard for residual analysis is not designated in Japanese Food Sanitation laws. Generally speaking, such a test for pesticide residue analysis does not need to be carried out, and it actually was not carried out in any laboratory for the pesticide analysis. Furthermore, a report for water content or LOD of pesticide standard has not been published. Since the obtained result of the standard deviation in pesticide residue analysis is often a quite larger value than the standard deviation in the purity test of medical drug mentioned in the Japanese Pharmacopoeia XIV, it seems that the analyst for pesticide residue analysis may ignore the slight water within 1%. However, some kinds of hygroscopic pesticides include relatively a large amount of water, or pesticide standards recrystallized from organic solvent can contain a large amount of organic solvent.

TGA uses a thermogravimeter that consists of a microbalance and a heating furnace surrounding sample pan of the microbalance. As an advantage, the required minimum sample weight is small (generally 1–20 mg) with a high reproducibility.[2–5)] As a drawback, the measurement time is relatively long and a liquid sample is not proper for LOD using TGA. KF measures the water content in a sample.[1,5–7)]

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In the present study, we used a coulometric Karl Fisher titrater to measure the small amount of pesticide standard. As an advantage of the coulometric KF, the required minimum sample weight is small (generally 1–10 mg) with a high reproducibility in a short time. As a drawback, an insoluble material in the Karl Fisher reagent and any material interfering with the Karl Fisher reaction are not adequate to KF.[7]

In the present study, to investigate the actual situation of the water content or LOD value of commercial pesticide standards, 40 pesticide standards were determined by KF and 24 pesticide standards were determined by TGA. Furthermore, the applicability of KF and TGA for pesticide standards was also discussed.

MATERIALS AND METHODS

Materials —— When we studied the water content and LOD of the pesticide standards, mainly selected were highly water-soluble pesticides, hygroscopic pesticides or pesticides including characteristic metals in their structures. Thiocarbamate pesticides, ferbam, mancozeb, zineb, ziram and maneb, have chelated metal atoms in their structures, and they show low water solubility. Chlormequat chloride, bromacil and monocrotofos are labeled as hygroscopic pesticides by their manufactures. Table 1 summarizes the water solubility, characteristic atoms, state and melting point of the target pesticides.[8]

Pesticide standards of acephate (lot#KPJ9484), alloxydim sodium salt (lot#DPK9051), asulam (lot#HCH9592), azocyclotin (lot#JCQ9596), bispyribac sodium salt (lot#YWF9198), chlormequat chloride (lot#TWK9018), cyprodinil (lot#YWH 9695), trichlorfon (lot#TLF9321), sodium dimethyl dithiocarbamate dihydrate (lot#HCJ9429), diquat dibromide monohydrate (lot#JSR9763), dichloropropionic acid sodium salt (lot#HPQ9446), fenthion (lot#YWE9710), fosetyl (lot#HCR9072), fosthiazate (lot#YLL9755), hydroxyisoxazole (lot#HCJ9420), iminoctadine albesilate (lot#JCM9150), iminoctadine triacetate (lot#RLP9650), methamidophos (lot#HCK9413), methomyl (lot#HCQ9546), monocrotophos (lot#MCE9478), oxadixyl (lot#AWN 9396), oxine cupper (lot#HCL9865), paraquat (lot# EPQ9806), thiuram (lot#HCL9891), triflumizole (lot#DSP9296) and zineb (lot#KLP6974) were purchased from Wako Pure Chemical Industries, Ltd., (Osaka, Japan). Pesticide standards of bromacil (lot#13400), dicamba (lot#13430), dimethoate (lot# 13430), ferbam (lot#93560), glufosinate ammonium (lot#10530), imazalil (lot#02410), malathion (lot# 02360), mancozeb (lot#12750), maneb (lot#21460), metalaxyl (lot#12000), vamidothion (lot#10530) and ziram (lot#00260) were purchased from Riedel-de Haën (Hannover, Germany). The pesticide standard of formamidine hydrochloride (JCK06668) was purchased from Hayashi Pure Chemical Ind. Ltd. (Osaka, Japan). The pesticide standard of emamectin benzoate (lot#921/1) was obtained from Novartis Agro (Tokyo, Japan).

Measurements —— In order to minimize the scatter of the measured values due to the absorption of moisture by samples with passage of time, measurements by TGA and KF were performed at the same time when possible.

TGA: TGA was carried out at the heating rate of 5°C/min using a Shimadzu TGA-50 thermogravimeter attached to a tube purging any toxic gases to a draft chamber. Weight losses were observed from room temperature to about 250°C. The temperature scale of the thermogravimeter was calibrated using the Curie point of metal nickel (purity, 99.99%) as 353°C, the mass scale being calibrated by the use of standard weights. Dry nitrogen gas was used as the atmosphere and the flow rate was controlled at 20 ml/min. Approximately 10 mg of the powder sample was placed on aluminum pans (6 mm inner diameter and 5 mm height) without sealing, and then the measurements were immediately performed.

The pesticides whose melting point is less than 100°C was basically not measured by TGA, because free water that adheres on all surface of the pesticide is hard to volatilize until about 100°C. Reference measurements were performed using empty pans and all data corrected by subtraction of the reference from the observed values.

KF: The titrimetric determinations of water were performed at room temperature (about 20°C) using a Hiranuma AQ-6 Karl-Fisher moisture content meter equipped with a coulometric titration system. The Karl-Fisher reagents, Hydranal® Aqualite® RS as the catholite and Aqualite® CN as the anolite were purchased from Riedel-de Haën. All target pesticide standards were weighed using a Metler M3 microbalance, and measurements were immediately carried out.

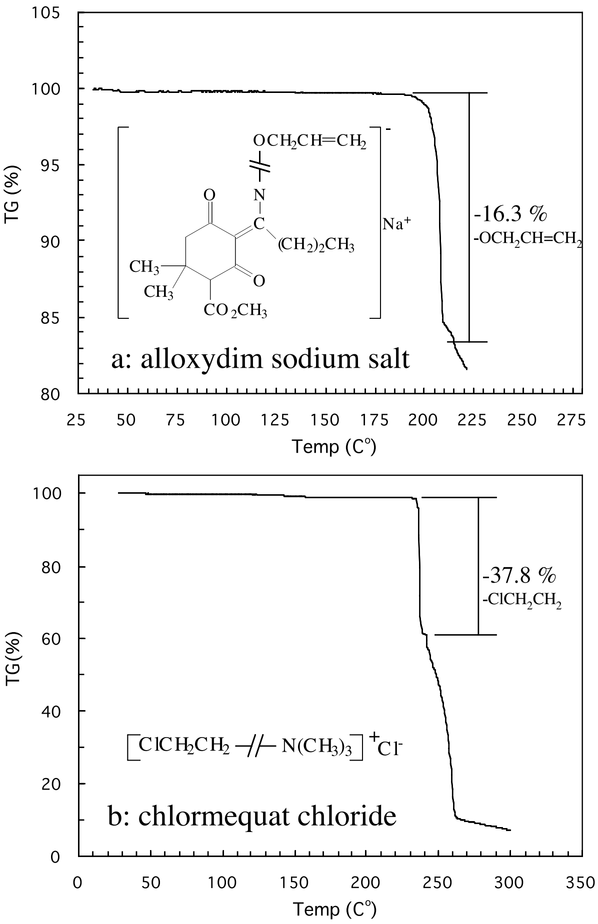

Fig. 1. Typical TGA Curves for Alloxydim Sodium Salt and Chlormequat Chloride

Numerals in these figures indicate the weight losses for their decompositions in percent.

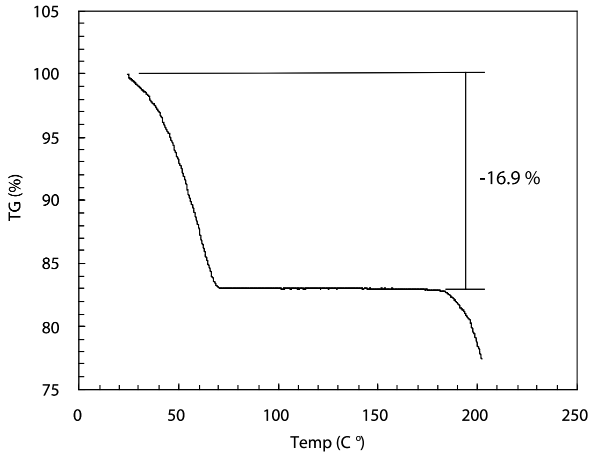

Fig. 2. Typical TGA Curve for Dichloropropionic Acid Sodium Salt

Numeral in this figure indicates the weight losses for its waters in percent.

RESULTS AND DISCUSSION

Shape of TGA Curve

TGA does not observe only LOD during heating, but a decomposition of compounds. Figure 1 shows some TGA curve patterns for alloxydim sodium salt and chlormequat chloride. In Fig. 1a, the weight of alloxydim sodium salt slightly decreased until about 160°C by the volatilization of water, gradually decreased until about 195°C and then abruptly decreased above about 200°C due to the decomposition of alloxydim sodium salt. It is assumed that the decomposition up to 210°C arises from desorption of $OCH_2CH{=}CH_2$. In Fig. 1b, the weight of chlormequat chloride slightly decreased until about 150°C by the volatilization of water and then abruptly decreased above 235°C due to the decomposition of chlormequat chloride. It is assumed that the decomposition up to 240°C arises from the desorption of $ClCH_2CH_2$.

To express the calculation method of LOD using TGA, a typical TGA curve for dichloropropionic acid sodium salt is shown in Fig. 2. During the initial stage, the weight loss is very small, followed by an increase with the rise in temperature. After a final steep drop, the weight loss stops at about 70°C and the weight becomes constant in spite of increasing the temperature to approximately 180°C. The abrupt decrease in the weight above 180°C can be ascribed to the degradation of the pesticide itself. The difference between the initial weight and the final plateau portions is evaluated as the LOD value. Some pesticides that have such a TGA curve with a plateau portion can be reasonably estimated (Figs. 3a–3c), however, most pesticides used in this study did not have a plateau portion in their TGA curves (Figs. 3d–3f). In Figs. 3d–3f, the LOD values are estimated by the differences between the initial weight and the weight just before the abrupt decrease in weight arising from the decomposition of the pesticides.

LOD Values by TGA and Water Content by KF

Table 1 summarizes the LOD values by TGA and the water content values by KF for the pesticides. The obtained values by both TGA and KF showed relatively low standard deviations. The LOD values and the water content values of most pesticides were within 1%. However, the LOD values of dichloropropionic acid sodium salt, diquat dibromide, paraquat, mancozeb, sodium dimethyl dithiocarbamate, iminoctadine triacetate, and formamidine hydrochloride were more than 2.00% and the LOD values

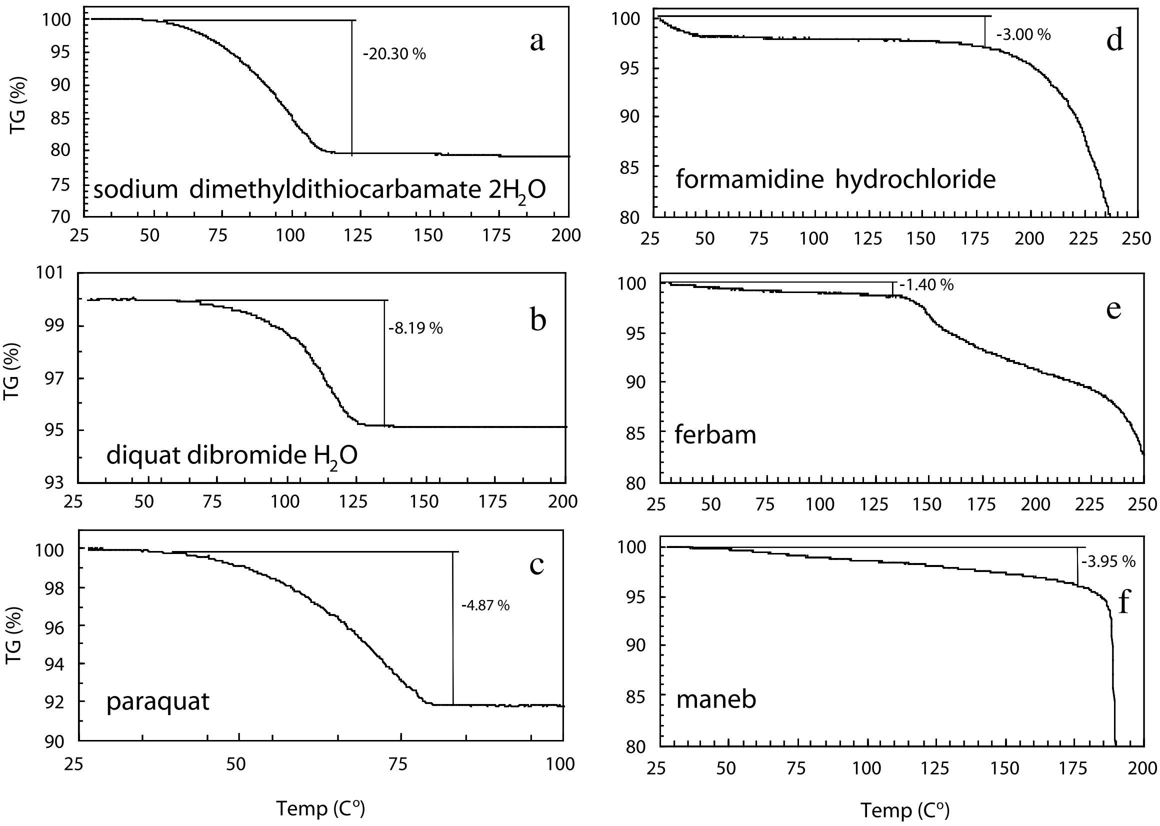

Fig. 3. Typical TGA Curves for 6 pesticide Standards
Numerals in these figures indicate the weight losses for their waters in percent.

of glufosinate ammonium, bromacil, chlormequat chloride, ferbam and zineb were between 1.00 and 2.00%. The water content values of monocrotophos, chlormequat chloride, dichloropropionic acid sodium salt, diquat dibromide, paraquat, ferbam, mancozeb, sodium dimethyl dithiocarbamate, iminoctadine triacetate, and formamidine hydrochloride were more than 2.00% and the water content values of fosthiazate, glufosinate ammonium, methamidophos, bispyribac sodium salt, zineb and emamectin benzoate were between 1.00 and 2.00%.

From the LOD data, we can estimate the number of hydrated waters in one pesticide molecule. If all the weight loss on LOD was assumed to be water, one molecule of dichloropropionic acid sodium salt and sodium dimethyl dithiocarbamate had 1.86 and 2.03 molecules of water in them, respectively. Therefore, it was thought that they could exist as dihydrate. One molecule of diquat dibromide and paraquat chloride had 0.98 and 0.92 molecules of water in them, respectively. Therefore, it was thought that they could exist as monohydrates.

Comparison between TGA Value and KF Value

Figure 4 shows a correlative comparison of the LOD values by TGA and water contents by KF. If the point of a pesticide is near the dotted line, it is regarded as a good correlation between the set of values, and such a good correlation is evident for pesticides containing water as a volatile contaminant. However, in some pesticides, the set of values showed considerably different values. For ferbum, chlormequat chloride and ziram, the KF values were considerably higher than the TGA values. It seems that the components of the pesticides molecules reduced the iodine, so that a high water content values were obtained. Inversely, KF value of bromacil was lower than the TGA value. It seems that bromine of the bromacil molecule oxidized the iodide to iodine, so that a low KF value was obtained. Generally speaking, the KF method is easy to measure pesticides, because most pesticides are soluble in organic solvents including KF reagent. However, the obtained data should be carefully considered in the application of KF to pesticide, because the KF method is a redox reaction and there are possibility of a chemical reaction between the pesticide and the

Table 1. Descriptions of Pesticides[8)] and Result of Weight Losses by TGA and Water Contents by KF

	Water Solubility[a)]	Characteristic atom	State[b)]	Melting point (°C)	LOD by TGA (%)[c)]	Water content by KF (%)[c)]
Organophosphorus						
Acephate	790		S	88–90	nd	0.14 ± 0.01
DEP	120		S	78.5–84	nd	0.01 ± 0.00
Dimethoate	23.3		S	49	nd	0.05 ± 0.00
Fenthion	0.0042		L	−80	nd	0.07 ± 0.01
Fosetyl	120		S	200 (dec.)	0.73 ± 0.01	0.67 ± 0.08
Fosthiazate	9.85		L	not available	nd	1.10 ± 0.09
Glufosinate ammonium	1370		S	215	1.12 ± 0.00	1.38 ± 0.03
Malathion	0.145		L	2.85	nd	0.21 ± 0.02
Methamidophos	up to 200		S	44.9	nd	1.07 ± 0.09
Monocrotophos	1000		S	54–55	nd	2.07 ± 0.21
Vamidothion	4000		S	43	nd	0.53 ± 0.04
Harbicides						
Alloxydim sodium salt	2000		S	185.5 (dec.)	0.39 ± 0.02	0.28 ± 0.00
Asulam	5		S	142–144 (dec.)	0.26 ± 0.02	0.20 ± 0.00
Bispyribac sodium salt	733		S	223–224	0.96 ± 0.03	1.54 ± 0.03
Bromacil	807		S	157–160	1.34 ± 0.02	0.10 ± 0.00
Chlormequat chloride	up to 1000		S	235		
				245 (dec.)	1.05 ± 0.04	4.14 ± 0.10
Dicamba	6.5		S	114–116		
				200 (dec.)	0.11 ± 0.03	0.08 ± 0.00
Dichloropropionic acid sodium salt	900		S	191 (dec.)	16.90 ± 0.38	17.49 ± 0.50
Diquat dibromide H_2O	700		S	> 300 (dec.)	4.87 ± 0.23	4.63 ± 0.27
Metalaxyl	8.4		S	63.5–72.3	nd	0.04 ± 0.00
Paraquat	10000		S	300 (dec.)	8.19 ± 0.03	7.91 ± 0.52
Carbamates						
Ferbam	0.13	Fe	S	180	1.37 ± 0.02	7.03 ± 0.79
Mancozeb	0.02	Mn	S	192–204 (dec.)	2.15 ± 0.01	2.67 ± 0.30
Methomyl	57.9		S	78–79	nd	0.01 ± 0.00
Metolcarb	2.69		S	76–77	nd	0.03 ± 0.01
Sodium dimethyl dithiocarbamate $2H_2O$	not available		S	120	20.30 ± 0.28	23.14 ± 0.34
Thiuram	0.018		S	155–156	0.04 ± 0.00	-0.08 ± 0.00
Zineb	0.01	Zn	S	157 (dec.)	1.29 ± 0.03	1.24 ± 0.18
Ziram	0.00003	Zn	S	246	0.58 ± 0.02	3.73 ± 0.45
Fungicides						
Cyprodinil	20		S	75.9	0.23 ± 0.00	0.14 ± 0.01
Hydroxyisoxazole	85		S	86–87	nd	0.02 ± 0.00
Imazalil	0.18		S	52.7	nd	0.05 ± 0.00
Iminoctadine albesilate	0.006		S	92–96	nd	0.38 ± 0.03
Iminoctadine triacetate	764		S	143.0–144.2	2.02 ± 0.09	2.05 ± 0.10
Maneb	insoluble	Mn	S	192–204 (dec.)	3.95 ± 0.01	4.06 ± 0.12
Oxine cupper	0.00007	Cu	S	270 (dec.)	0.10 ± 0.00	0.14 ± 0.04
Triflumizole	12.5		S	63.5	nd	0.00 ± 0.00
Acaricides						
Azocyclotin	0.0012	Sn	S	210 (dec.)	0.34 ± 0.00	0.23 ± 0.03
Emamectin benzoate			S	141–146	0.94 ± 0.04	1.35 ± 0.01
Formamidine hydrochloride	not available		S	79–85	2.97 ± 0.02	4.99 ± 0.12

a) The water solubility is defined as g/l at a temperature at 20 or 25°C. *b*) Liquid or solid at room temperature are defined as L and S, respectively. *c*) Average from three runs ($n = 3$). nd means not done.

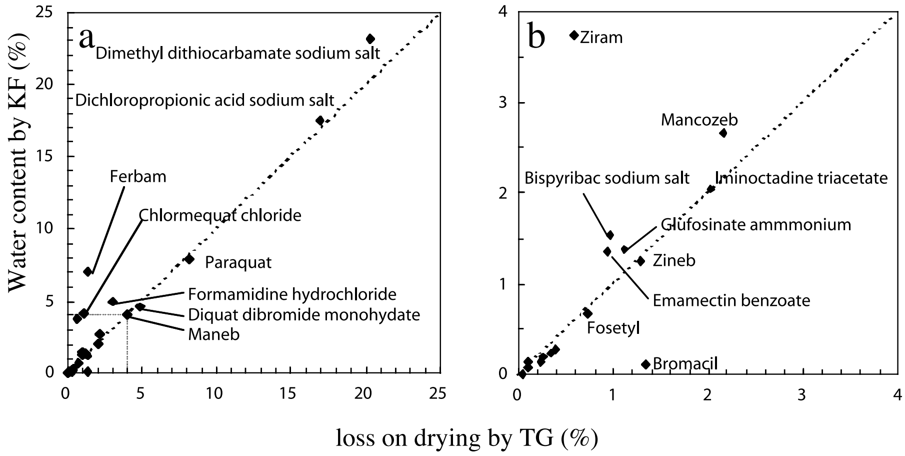

Fig. 4. Comparison of Values for LOD by TGA and Water Content by KF
Figure “b” is an enlargement of “a.” Values in the figure are the same as the values in Table 1.

KF reagent.

In conclusion, the water content or LOD values of most tested pesticides were within 1%, therefore, they are regarded as negligible values within the limit of error for residual pesticide analysis. However, since some pesticides had a relatively large amount of water, the water contents or LOD values of such pesticides should be carefully considered when doing the pesticide residue analysis.

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