KARL FISCHER TITRATION AS AN ALTERNATIVE METHOD FOR DETERMING THE WATER CONTENT OF INDONESIAN SPICES

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ABSTRACT

Karl Fischer Titration (KFT) is a well established and effective direct primary method to determine water content in various materials. It is based on a specific chemical reaction and it differs principally from the drying and distillation methods. The KFT was introduced as an alternative method to determine the water content in some Indonesian spices (clove, coriander, ginger and white pepper), which generally contain appreciable amount of volatile compounds to distract accurate moisture. The samples used were prepared by cutting and grinding with a morser. The KFT system used was one-component reagent with methanol as working medium. The samples were introduced into a KFT titration cell and titrated directly with the KFT reagent. The extraction time of determination was 60 seconds. The determination of the water content took approximately 10-20 minutes. The distillation and drying method served as control or reference method. The distillation methods which used was a mixture of toluene and xylene 95:5 (v/v) took 2 hours. The drying method was conducted at temperature of 105°C for 3-4 hours.

INTRODUCTION

Water determination is one of the most important and most widely used in the food industries. High moisture can cause negative effect on the stability and quality of food. The water content causes many problems, e.g. in the evaluation of material's balance or of processing losses, in determining the nutritive value of foods, in expressing results of analytical determinations on a uniform basis, etc (Pomeranz and Meloan, 1994).

Three kinds of moisture and water determination methods were conducted to determine the water and moisture content of Indonesian spices, which were clove, coriander, ginger and white pepper. The methods were drying, distillation and Karl Fischer titration.

The dyring oven method based on loss on drying (LOD) due to heating necessarily involves in empirical choice of type of oven and temperature and length of the drying. In the practice, heating of the sample can cause decomposition reaction of organic matters, which may produce volatile components and water. Also the volatile components were calculated as water.

The distillation with boiling liquid provides an affective means of heat transfer, the water is removed rapidly and the determination is made in an inert atmosphere that minimizes danger of oxidation. But some difficulties may can be faced in this method, e.g. relatively low precision of receiving measuring devices, difficulties in reading of meniscus, adherence of moisture droplet to glass, overboiling of the liquid, solubilty of water in the distillation liquid, incomplete evaporation of water and underestimation of moisture content, and distillation of water-soluble components.

The Karl Fischer titration has a special advantage that the water reacts selectively in a two step chemical reaction. In methanol as working medium the Karl Fischer reaction runs as follows:

$$CH_3OH + SO_2 + R_3N \quad R_3NH^+ + CH_3OSO_2^- \; R_3NH^+ + CH_3OSO_2^- + I_2 + H_2O \; 3\,R_3NH^+ + CH_3OSO_3^- + 2\,I^-$$

$$CH_3OH + SO_2 + I_2 + H_2O + 3\,R_3N \cdot CH_3OSO_3^- + 3\,R_3NH^+ + 2\,I^-$$

R_3N is base. The historically used pyridin was replaced by other bases, like imidazole. Methanol serves as reactant as well as working medium (Scholz, 1984).

The Karl Fischer titration can be done with two difference standard procedures; volumetric and coulometric titration. The volumetric titration can be divided into two kind of titrations, the volumetric titration using an one-component reagent and using a two-component reagent. The one-component reagent contains all of reactants, i.e iodine, sulfur dioxide and imidazole, dissolved in a suitable alcohol. As working medium in this system is methanol. The two-component system is separated in two solutions; a solvent contains sulfur dioxide and imidazole in methanol and a titrant consists iodine with pre-determined titre. The coulometric titration needs two solutions, an anolyte and a catholyte. The anolyte is a modified Karl Fischer reagent containing iodide instead of iodine. The Karl Fischer

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reaction occurs in the anolyte.The catholyte is a reaction partner of the anolyte, which is special formulated to meet the requirements of the cathodic reduction (Scholz, 1984; Scholz, 1995).

Because of their matrices samples would be determined by special variants of the Karl Fischer titration. Some variants of this method could be mentionend as follows; addition of alcohols, addition of chloroform, addition of formamide, methanol-free working media, neutralization of bases, neutralization of acids, titrations at low temperature, titration at elevated temperature, titration in boiling methanol, the combination method with a oven and determination of water in gases (Scholz, 1995).

In this research the standard method of the Karl Fischer titration by room temperature (one-component system) was conducted and compared with results of the distillation and the drying oven method.

METHODS

The indonesian spices were clove, coriander, ginger and white pepper, that were usually sold in traditional markets in Surakarta (Midlle Java). They were dried spices except ginger, which was fresh. The drying process was normally a sun drying process. Sample preparation for the water determination were cutting and grinding with morser.

The drying method was done with a drying oven with a temperatur of 103 °C for 3-4 hours. The distillation apparatus of ISO 939-1980 was used. The distillation liquid was a 200 ml mixture of toluene and xylene 95:5 (v/v). The distillation duration was 2 hours.

Hydranal-Composite 5 as titration agent and methanol as working medium, were from Riedel-de Haen, Seelze, Germany. Distilled water served as standard for the determination of the water equivalent or titre of the Karl Fischer reagent.

The titrations were carried out with the KF-Titrino 701 with Ti-Stand 703 with magnetic stirrer, the exchange unit 696 (20 ml). The titrator was equipped with a double platinum electrode to determine the end point of titration. All of these equipments were from Metrohm, Herisau, Switzerland. An analytical balance A 210 P from Sartorius, Goettingen, Germany was used for mass determination. Time was measured with a digital stop watch.

Determination of the water equivalent

The water equivalent or titre was determined by titrating known amounts of distilled water (20-40 mg).

Determination of drift

In course of time a slight consumption of reagent to keep the titration cell dry is always observed. This so-called drift is due to the water penetrating through the tubes and joint. In some rare cases water could be produced by side reactions of components in already titrated samples with the Karl Fischer reagent. For very precise water determination, especially for those which take a long time the reagent consumption due to the drift should be deducted from the result. The drift can expressed in µl/min or in mg H_2O/min.

To measure the drift, 25 ml of methanol were dried by usual pre-titration. Then a stimulated titration without sample was started. The duration was fixed to 30 minutes, by imposing a corresponding extraction time. During this time, the cell is kept dry, but the titration is not stopped, even if the end point criteria should be fulfilled.

Determination of the water content of spices

To determine the water content in spices, 25 ml of methanol were pre-titrated. After which the sample (250-400 mg) was introduced to the titration cell.

The extraction time of 300 seconds was programmed. As end indication the bivoltametric method with a polarizing current of 50 µA and a final tension of 250 mV was chosen. The determination was ended automatically, when the drift reached a value below 10 µl/min.

As reference method to determine the water content in spices an azeotropic distillation method was used. The 10 g sample of spices were weighed and boiled in a boiling flask under a distillation equipment equipped with cooler for 2 hours. Two hundreds ml of a mixture of toluene:xylene 95:5 (v/v) served as boiling reagent.

Determination of moisture or loss on drying (LOD)

The moisture content was determined by the drying oven method, because during the drying process in the oven not only the water but the volatile components were evaporated too. The 2,0 - 2,5 g of spices were weighed and dried in the oven by 103 - 104 °C for two hours.

RESULT AND DISCUSSION

Tabel 1. Result of the determination of titre of 5 Karl Fischer reagents (n = 10)

Reagent	Titre (mg/ml)	s (mg/ml)	V (%)
1	5.1977	0.0439	0.84
2	5.2800	0.0441	0.92
3	5.2722	0.0427	0.81
4	5.1633	0.0388	0.75
5	5.1454	0.0332	0.65

s : standard deviation ; V: varianzcoefficient; n : sum of the determination

Tabel 2. Result of drift (n = 2)

Determination	Drift (mgH_2O/min)
1	0.024
2	0.030
3	0.022
4	0.031

Tabel 3. The loss on drying (LOD) content of spices (*drying oven method*) (n = 5)

Sample	LOD (%)	s (%)
Clove	11.14	0.265
Coriander	11.50	0.252
Ginger	88.03	3.060
White pepper	13.81	0.061

Tabel 4. The water content if spices determined by distillation andKarl Fischer titration (n = 5)

Sample	Distillation		Karl Fischer	
	Water content (%)	s (%)	Water content (%)	s (%)
Clove	5.96	0.494	7.52	0.594
Coriander	7.65	0.371	10.08	0.516
Ginger	81.11	0.832	86.43	0.594
White pepper	11.94	0.665	14.99	0.064

Tab. 5. Suggested water content of whole dried spices

Spices	Water content (%)[a]	Water content (%)[b]
Clove	5.0 - 8.0	max. 8.0
Coriander	5.0 - 9.0	max. 9.0
Ginger	6.0 - 9.4	max. 12.0
Pepper white	9.0 - 11.0	max. 14.0

[a] (Gerhard, 1990) and (Farrel, 1990)

[b] Food and Drug Adiministration (FDA) in (Taitner & Grenis, 1993)

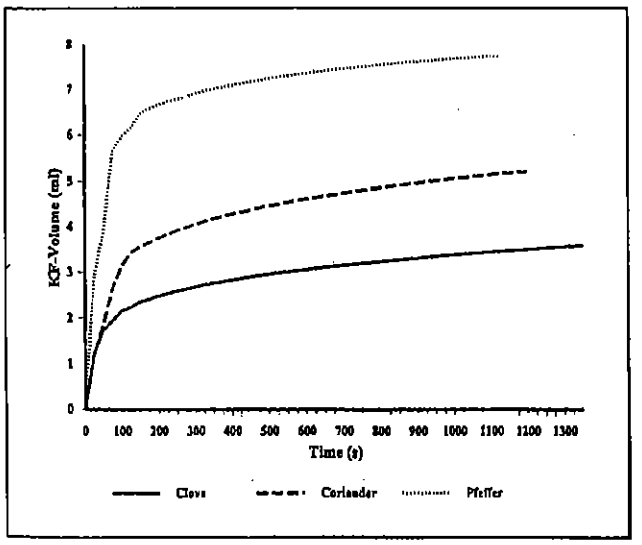

Figure 1. Karl Fischer titration curves of dried clove, coriander and pepper white one-component reagent - direct titration - extraction time of 60 s

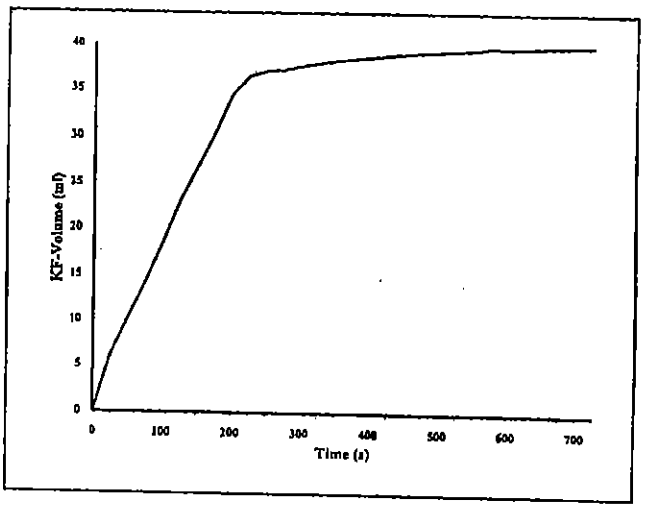

Figure 2. Karl Fischer titration curve of fresh ginger one-component reagent - direct titration - extraction time of 60 s

Based on the result in table 3, the loss on drying were higher than the water content by the distillation method, which prevails as a water content reference method for the spices. The used temperatur of drying oven method caused decomposition reactions, that could produce small amount of water. Under this temperature volatile components, such as volatile oils, were also evaporated. So the table 3 did not show the moisture content, but the content of loss on drying. The drying oven method are not used as a reference method to determine the water content of spices except by capsicum products (Taitner & Grenis, 1993)

Comparing the water contents between by the distillation and the Karl Fischer method in table 4, it could be stated, that the results of the Karl Fischer method were higher than by the distillation method. The lower water content of the distillation method could be explained because of the disadvantages of this method, e.g. difficulties in reading the meniscus, low precision of the receiving measuring devices, etc. The distillation method needs also more time to determine the water content in the spices, for example 15 minutes to prepare the sample, 10 minutes to boil the solution, 2 hours to distillate the sample, and 15 minutes to cool down the apparatus.

Because of these disadvantages of the distillation method, the Karl Fischer titration was introduced as the reference method to determine the water content of Indonesian spices. The results were relative more accurate and higher than the distillation method. The Karl Fischer titration needed maximal 25 minutes to determine the water content, which depended on the kind of the spices. To assure the determination by the Karl Fischer titration, the titration curves of these determinations were showed in Fig. 1 and 2. They depicted, that the titrations ran well but some interferences appeared during the titration, which could be eliminated. These determinations could be made faster and

more precise and accurate, if some variants of the Karl Fischer titration were utilized, such as titration at elevated temperature.

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