

## Analysis of Water Content in Soap Formulation Using Fourier Transform Infrared (FTIR) Spectroscopy

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**Abstract:** A rapid, sensitive, and non-time consuming method of Fourier Transform Infrared (FTIR) Spectroscopy at wave number of 3600 – 3200  $\text{cm}^{-1}$  has been used for determination of water content in soap samples. The developed method was comparable to AOCS Ca 2c-25 method. A chemometrics partial least square (PLS) was used for constructing a calibration model. The 'leave-one-out' technique was used for cross validation. The correlation between water content using FTIR and AOCS in soap formulation existed a good relationship with coefficient of determination ( $R^2$ ) value of 0.923. This study revealed that FTIR spectroscopy combined with the PLS calibration technique is fast and accurate for quantitative analysis of water content in soap samples.

**Key words:** FTIR spectroscopy, partial least square, soap, water content

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### INTRODUCTION

Fats, either derived from vegetable oil like virgin coconut oil (VCO) or from animal fats such as mutton and lard, are raw materials used in making an industrial soap. Chemically, soap is sodium-fatty acid produced by saponification reaction using aqueous-alkali hydroxide such as sodium hydroxide and potassium hydroxide. Soap functions as an anionic surface active agent (surfactant) used to clean and wash skin and clothing <sup>[1]</sup>.

Analytical methods for determination of water and volatile matters have been developed in order to provide an accurate result of moisture content. Such official methods has been used by The American Oil Chemists' Society (AOCS) to analyze water involving evaporation of moisture from samples, such as hot-plate (Ca 2b-38) by heating samples in a Beaker with gentle agitation on hot plate until foaming stops and initial smoking begins, air oven (Ca 2c-25) which use oven to evaporate water at  $101 \pm 1^\circ\text{C}$ , and vacuum oven (Ca 2d-25) using a vacuum not exceed 100 mm of mercury at temperature of 20 – 25  $^\circ\text{C}$  above the boiling point of water. These methods were time consuming because these involve several times of measurements until samples reach weight constant AOCS also used The Karl Fischer method to determine the water content which is not involving heat in its analysis but use hazardous chemicals like pyridine, sulfur dioxide, chloroform, and anhydrous methanol <sup>[2]</sup>.

Another official method for water determination can be seen in Union of Pure and Applied Chemistry (IUPAC) <sup>[3]</sup> using distillation method, however, this method is not accurate enough for values of less than 0.05% moisture.

Fourier transform infrared (FTIR) spectroscopy is a technique that can be easily adapted for use by untrained personnel in laboratories or on factory floor. A particular attraction of FTIR is the easy of sample presentation <sup>[4]</sup>. It had been used to determine water content in fat and/or in high-fat products <sup>[5]</sup>. Furthermore, Che Man and Mirghani <sup>[6]</sup> also developed FTIR spectroscopic technique for determination of moisture content of crude palm oil (CPO). However, there is no report related to its use for determination of water in soap formulation, derived from fats or oils. Therefore the objective of this study was to evaluate FTIR spectroscopy as an alternative method for water determination in soap formulations.

### MATERIALS AND METHODS

**Materials:** VCO was obtained from local market in Jogjakarta, Indonesia. VCO was dried from water residue in oven for  $3\text{hr} \pm 1$  at  $105^\circ\text{C}$ . Drying was repeated several times such in a way, until a constant weight was reached after cooling at ambient temperature in a desiccator containing activated silica gel. Sodium hydroxide, sodium carbonae, and sodium chloride were obtained from E.Merck (Darmstadt Germany).

## Methods:

**Calibration and Validation:** For partial least square (PLS) calibration, a series of standard was prepared by spiking VCO with bidistilled water from 0 – 25.0 % w/w. Samples were tightly covered, shaken vigorously using Vortex (Heidolph, Germany) to ensure the homogeneity of samples.

A set of ten laboratory samples was prepared consisted of 60 m VCO; 26 mL aqueous sodium hydroxide 8M; 9 ml aqueous sodium carbonate 10 %; 2.5 g sodium chloride with different amount of water in the final formulation.

The water content of each sample was further analyzed using FTIR spectroscopy and AOCS air oven method Ca 2c-25.

## Analysis of Water Content Using AOCS Air Oven

**Method:** Approximately 5 gram of samples was accurately weighed using analytical balance (sensitivity 0.1 mg) into dried, tared moisture dish and dried in the oven (Memmert, Germany) for 2 hr at  $101 \pm 1$  °C and repeated until a constant weight (difference between two measurement not exceed 0.5 mg/g of sample) was reached.

**FTIR Instrumental Analysis:** FTIR spectrometer Nicolet 6700, supplied by Thermo Nicolet Corp., Madison, WI, equipped with a detector of deuterated triglycine sulphate (DTGS) was used in instrumental analysis. OMNIC software (Version 7.0 Thermo Nicolet) for operating system was used to afford FTIR spectra of samples. The samples were located in contact with attenuated total reflectance (ATR) element (ZnSe crystal) at room temperature. FTIR spectra were collected in wavenumber  $4000 - 650$   $\text{cm}^{-1}$  with 32 scanning and at resolution of  $4$   $\text{cm}^{-1}$ . Sample spectra were recorded as absorbance values at each data point in triplicate.

**Statistical Analysis and Validation:** A software package of TQ Analyst™ from Thermo electron Corporation was used to construct a calibration and validation models using partial least squares (PLS). In order to verify calibration model, a cross validation procedure was carried with “leave one-out” technique. The validity criteria used are the values of root mean standard error of cross validation (RMSECV) and coefficient of determination ( $R^2$ ). The validation was further investigated using parameters of mean difference (MD) and standard deviation of difference (SDD) for method accuracy and precision, respectively.

## RESULT AND DISCUSSIONS

**Spectrum Analysis of Water:** The presence of water can be easily identified by observing a broad peak at  $3600 - 3200$   $\text{cm}^{-1}$ , which is characteristics for vibration of –OH stretching. Figure 1 showed FTIR spectrum of

free- water VCO (A) and a soap containing water (B). The great difference of two spectra was clearly observed at regions of  $3383$   $\text{cm}^{-1}$  which is caused by vibration of –OH stretching of hydrogen bonding. The presence of –OH vibration can be also seen at a frequency of  $1644$   $\text{cm}^{-1}$  as reported by van de Voort *et al.* [5], Safar *et al.* [7] as well as by Che Man and Mirghani [5]. This peak was absent in VCO spectrum, therefore it can be stated that it is solely due to water used as a medium to dissolve sodium hydroxide in making soap formulation. These frequencies ( $3383$   $\text{cm}^{-1}$  and  $1650$   $\text{cm}^{-1}$ ) were used for calibration model and compared in term of  $R^2$  and RMSEC values.

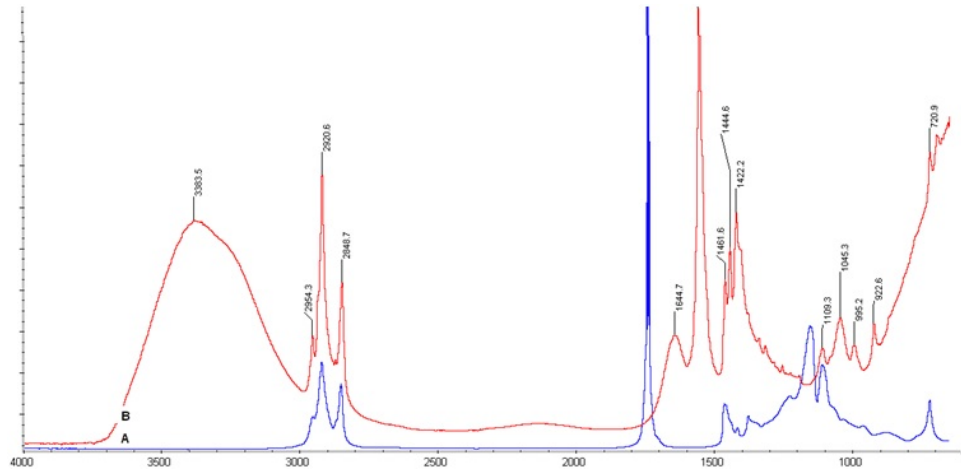
**Calibration and Validation:** Calibration and validation models were carried out using multivariate analysis of partial least square (PLS). PLS is a form of factor analysis where the spectra and concentration of samples are incorporated into the model in one step process [8]. PLS having an ability to use information of sample spectra from wide spectral frequencies and then correlate between spectral absorption change and its concentration of analytes, whilst concurrently computing other spectra which may disturb analyte spectra [9].

In PLS calibration model, evaluation of method linearity was performed in order to demonstrate a proportional relationship between responses (absorbance) versus analyte concentration of water over the working range. Frequencies at wavenumber of  $3600 - 3200$   $\text{cm}^{-1}$  and  $1660 - 1640$   $\text{cm}^{-1}$  were used for making a calibration curve. Figure 2 showed the increase of absorption of VCO spiked with known amount of water at frequencies  $3600 - 3200$   $\text{cm}^{-1}$ .

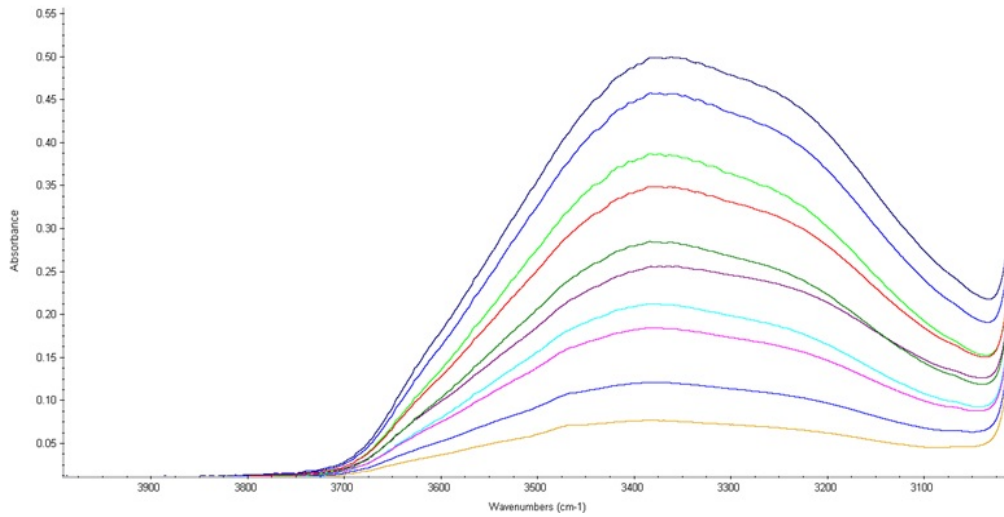
Using PLS at frequency  $3600 - 3200$   $\text{cm}^{-1}$  for calibration model,  $R^2$  value of 0.999 and RMSEC of 0.037 were obtained for relationship between actual value of water and FTIR predicted value (Figure 3). The linier regression equation together with the values of  $R^2$  and RMSEC of water in different wavenumber ranges was shown in Table 1

From table 1, it can be shown that PLS calibration of water at wavenumber of  $3600 - 3200$   $\text{cm}^{-1}$  was preferable to be used for prediction of water content in samples in terms of the highest of  $R^2$  value and the lowest of RMSEC value.

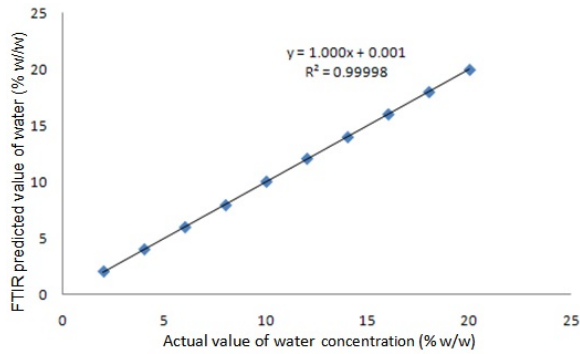
For the validation procedure, 20 independent VCO samples spiked with known amount of water was prepared to minimize the prediction error and to provide an estimate of the overall accuracy of predictions. Using the relationship between actual water content (%) in samples and FTIR predicted values of water content (%), a linier regression was obtained with equation  $y = 0.961x + 0.818$  and coefficient of determination ( $R^2$ ) of 0.981 with standard error of prediction (SEP) of 0.936 (Figure 4).



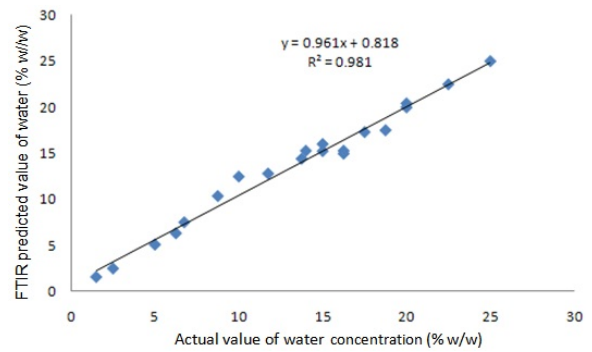
**Fig. 1:** FTIR spectra of pure VCO (A) and soap of VCO containing water at regions 4000 - 650 cm-1.



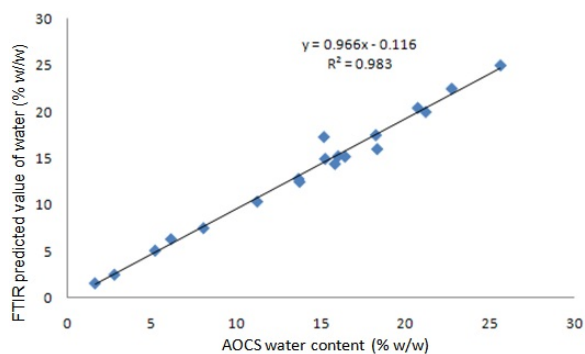
**Fig. 2:** The absorbance change of VCO spiked with different known concentration of water at regions 3600 - 3200 cm-1.



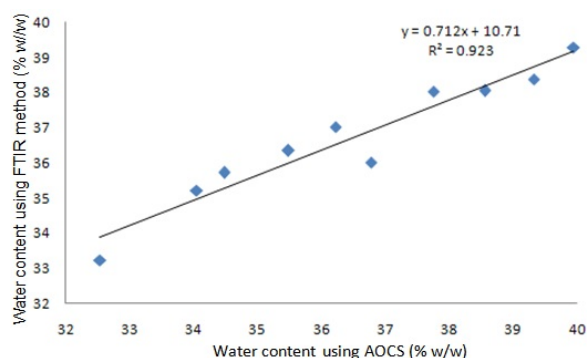
**Fig. 3:** Calibration curves obtained by partial least square (PLS) calibration. (A) water measured at wavenumber 3600 - 3200 cm-1.



**Fig. 4:** A plot of actual water contents versus FTIR predicted content of water (%) using PLS at frequencies 3600 - 3200 cm-1 obtained from cross validation.



**Fig. 5:** Correlation between water content determined using AOCS and using FTIR method.



**Fig. 6:** Correlation between water content determined using AOCS (x) and FTIR method (y) in soap formulation (each point was obtained from 3 replicates).

**Analysis of Water Content Using AOCS Air Oven Method Ca 2c-25:** After being analyzed using FTIR, VCO spiked with known amount of water was analyzed using AOCS air oven method Ca 2c-25. The correlation between water content using AOCS (x-axis) and that using FTIR (y) was shown in Figure 5. A good linear regression model was obtained ( $y = 0.966x - 0.116$ ) with  $R^2$  and SEP values of 0.983 and 0.879, respectively.

**Table 1:** PLS calibration for determination of water content and values of  $R^2$  and RMSEC at different frequency ranges

wavenumber in $\text{cm}^{-1}$	equation	$R^2$	RMSEC
Water at 3600 – 3200 $\text{cm}^{-1}$	$Y = 1.000x + 0.001$	0.999	0.037
Water at 1670 – 1540 $\text{cm}^{-1}$	$Y = 0.983x + 0.186$	0.983	0.747
Water at 3600 – 3200 $\text{cm}^{-1}$ and 1670 – 1540 $\text{cm}^{-1}$	$Y = 0.986x + 0.146$	0.986	0.662

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For method accuracy and precision, the statistical results computed from “leave-one-out” cross validation were mean difference (MD) and standard deviation of difference (SDD) for repeatability and accuracy, respectively. The values of MD and SDD were compiled in Table 2.

**Table 2:** statistical parameters of cross validation in term of MD and SDD values for determination of water content using FTIR and AOCS.

Statistics parameters	AOCS method	FTIR Method
MD <sub>accuracy</sub>	0.821	0.303
SDD <sub>accuracy</sub>	1.427	0.921
MD <sub>repeatability</sub>	0.935	0.724
SDD <sub>repeatability</sub>	1.632	0.875

Further analysis of water content was performed by preparing 10 samples of laboratory-made soap formulations consisted of VCO, sodium hydroxide, sodium carbonate, and sodium chloride with slight difference of water content. FTIR and AOCS air oven method were used to analyze these samples and its results were compared.

The correlation between water content using FTIR and AOCS in soap formulation existed a good relationship with  $R^2$  value of 0.923. Therefore, we proposed that FTIR can be used an alternative method to air oven method for determination of water content in soap formulation. The limitation of this method appeared if there are some soap ingredients containing hydroxyl group (-OH) in its molecules which will also absorb an infrared radiation in region 3600 – 3200  $\text{cm}^{-1}$ .

**Conclusions:** FTIR spectroscopy combined with chemometrics of PLS calibration can be used as an alternative to air oven method AOCS for quantification of water content in soap products. It is a possible alternative for fast, reliable, and inexpensive for routine determination at about 3 min.

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