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# METROLOGICALLY TRACEABLE DETERMINATION OF THE WATER CONTENT IN BIOPOLYMERS: INRIM ACTIVITY

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## Abstract

Water content in materials is a key factor affecting many chemical and physical properties. In polymers of biological origin, it influences their stability and mechanical properties as well as their biodegradability.

The present work describes the activity carried out at INRiM on the determination of water content in samples of a commercial starch-derived biopolymer widely used in shopping bags (Mater-Bi®). Its water content, together with temperature, is the most influencing parameter affecting its biodegradability, because of the considerable impact on the microbial activity which is responsible for the biopolymer degradation in the environment.

The main scope of the work was the establishment of a metrologically-traceable procedure for the determination of water content by using two electrochemical methods, namely coulometric Karl Fischer (cKF) titration and Evolved Water Vapour (E WV) analysis.

The obtained results are presented. The most significant operational parameters were considered and a particular attention was devoted to the establishment of metrological traceability of the measurement results by using appropriate calibration procedures, calibrated standards and suitable certified reference materials. Sample homogeneity and oven-drying temperature were found to be the most important influence quantities in the whole water content measurement process. The results of the two methods were in agreement within the stated uncertainties. Further development is foreseen for the application of cKF and E WV to other polymers.

## Keywords

Water content, metrological traceability, coulometric Karl Fischer titration, Evolved Water Vapour analysis, biopolymers

## Acknowledgments

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## 1. Introduction

The water content in materials is a fundamental parameter as it affects many physical and chemical properties. The determination of the water content has a great economic importance

as moisture influences, among others, the design of technological processes, the stability of industrial products, the shelf life of foodstuff, the calorific value of biomasses.

In particular, for polymers of biological origin, the water content may alter the stability, the mechanical properties and also the biodegradability of such materials.

The term biopolymer, or bioplastic, defines a wide class of polymers which originate from vegetal biomasses [1]. There are several types of biopolymers, which are used for the production of different materials having different mechanical, chemical and physical properties. Among these, there are starch, cellulose, biomasses and micro-organisms derived bioplastics [2].

In the present paper, the activity carried out at INRiM on the determination of water content in samples of a starch-derived commercial biopolymer widely used in shopping bags (Mater-Bi<sup>®</sup>) is described.

The determination of water content is usually carried out by the Loss on Drying (LoD) techniques (e.g. loss of weight, thermogravimetry): the sample is weighed before and after an oven-drying process, often at 105 °C, which might require several hours. The LoD techniques, however, present some limitations: they might fail in extracting all the water present in a certain material and, in addition, the measurement results might be biased from the presence of other volatile compounds or by the occurrence of chemical reactions [3]

Coulometric water determination represents a useful alternative to the LoD methods, and it can be coupled with the oven drying, for the analysis of the moisture evaporated from solid samples. For example, the Karl Fischer titration coupled with the oven technique for plastics is recommended in various International Standards [4,5].

Other techniques used as an alternative to coulometric water determination in polymer production are spectroscopic techniques such as Near InfraRed spectroscopy (NIR), which is used for the rapid and non-destructive analysis of plastics and biopolymers for the determination of mechanical and rheological properties [6] and it can be applied also to water content determination.

Few methods can be found in literature for the water content determination in polymers, mainly issued by the producers of dedicated instrumentation [7]. In this framework, the setting up of suitable and metrologically traceable procedure for water content determination is particularly needed.

The main scope of the work was the establishment of a metrologically-traceable procedure for the determination of water content by using two electrochemical methods, namely coulometric Karl Fischer (cKF) titration and Evolved Water Vapour (EWV) analysis, in the framework of the Joint Research Project SIB64 “METefnet - Metrology for Moisture in Materials” within the European Metrology Research Program (EMRP). This project aims, among other, at improving the metrological traceability for water content measurements by developing new measurement methods for the realisation and dissemination of the SI units and to strengthen the metrological infrastructure for moisture measurements in materials.

The material studied in the present work is a starch derived biopolymer, commercially identified as Mater-Bi<sup>®</sup>, produced by Novamont (Italy). This material complies with the European legislation concerning biodegradability of materials [8,9]. Starch is an organic compound made up of two polymers, amylose and amylopectin, having glucose as monomer and a great number of monomeric units. It is commonly present in vegetal products as potatoes, rice, corn or grain and it is widely used for the production of biopolymers, being a cheap, abundant and renewable material. Starch is biodegradable by micro-organisms and it can be combined with other material of biological origin [10]. Due to the hydrophilic nature of starch, the atmospheric humidity has a great influence on the mechanical properties of its derivatives [11].

The water content of Mater-Bi® is influenced by the absorption of the atmospheric water vapor as water molecules are continuously released and adsorbed from the material surface. When the rate of released and adsorbed water molecules is constant, a dynamic equilibrium is reached. The water content of Mater-Bi® increases with relative humidity, but it decreases when temperature increases; however, the main important parameter that determines its water content is the ambient humidity [10]. The atmospheric relative humidity and the correlated water content inside the material influence significantly the product biodegradability [12], thus playing, together with temperature, an important role on the microbial activity which is responsible for the material biodegradation [10].

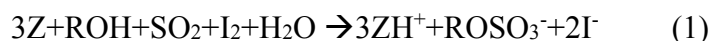
The novelty of the presented work concerns several aspects: it is based on two techniques selective for water, which allow the determination of the water content avoiding interferences from other volatiles, and this represents a great advantage with respect to the LoD methods; in addition the developed procedures guarantee the establishment of metrological traceability to the SI of the measurement results.

## 2. Materials and methods

Two coulometric methods, that are selectively sensitive to water, were considered and compared in the present work: coulometric Karl-Fischer titration (cKF) and Evolved Water Vapour (EWW) analysis.

### 2.1. Coulometric Karl Fischer titration

The cKF titration is a chemical direct method that uses a reaction selective to water based on the oxidation of sulphur dioxide (SO<sub>2</sub>):



where Z is a base and ROH is an alcohol, usually methanol.

The consumption of iodine (I<sub>2</sub>), which is stoichiometrically equivalent to the water present in the sample, is measured: I<sub>2</sub> is produced by the generating electrode from iodide (I<sup>-</sup>) and the end point is determined by a second electrode. The mass of water present in the sample is calculated from the amount of electric current (Coulomb) used for I<sub>2</sub> production.

The apparatus used at INRiM is a Karl Fischer (mod. c30, Mettler-Toledo, Switzerland) having a measurement range between 2 ppm and 5% of water. The system is equipped with a multi-sample carousel and a temperature-controlled oven. Solid samples are heated in the oven and the volatile compounds are brought into the KF titration cell for selective water determination.

### 2.2 Evolved Water Vapour analysis

The apparatus used at INRiM is an EWW analyser (mod. WDS 400, Sartorius, Germany), having a measurement range between 1 ppm and 40 % of water, with sample masses between 5 mg and 2 g. It is equipped with a phosphorous pentoxide-based (P<sub>2</sub>O<sub>5</sub>) coulometric detector. The instrument can differentiate among surface, capillary and crystallisation water. The samples are placed into a sample boat in the drying oven; a flux of dry air carries the water vapour to the sensor where P<sub>2</sub>O<sub>5</sub> absorbs the water vapour by forming phosphoric acid. The reaction product is then electrolysed to yield hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) and regenerating P<sub>2</sub>O<sub>5</sub>.

### 3. Results and discussion

#### 3.1 Application to Mater-Bi®

Samples of Mater-Bi® coming from common shopping bags distributed in local supermarkets were analysed with the two above mentioned coulometric techniques.

The experimental procedure included the following steps:

- optimisation of the instrumental parameters and of the sample manipulation;
- determination of the sample water content under metrological traceability conditions;
- uncertainty evaluation of the measurement results.

The measurements were carried out at 110 °C, a temperature comparable with the LoD techniques, and far enough from the melting temperature of Mater-Bi® at around 130 °C.

Concerning cKF, the operational parameters to be optimised during the method development were: duration of analysis, sample heating temperature, stirring rate, drift evaluation, ambient parameters (like relative humidity and temperature), repeatability, sample pre-treatment.

As for EWV, the main operational parameters checked and optimised during the method development were: efficiency of the desiccant system, stability of the background during the analyses, sample position in the oven, sample heating temperature, repeatability, sample pre-treatment.

#### 3.2 Calibration of the analysers

In order to calibrate both analysers, calibration standards at three different water levels were prepared by weighing several samples of a certified reference material (CRM) HYDRANAL® Water Standard KF-Oven 220-230 °C. The standard weighing was carried out following the double substitution scheme A-B-B-A using calibrated mass standards. For each water level, three different calibration standards were prepared. Table 1 reports the nominal masses of the CRM to be weighted ( $m_{CRM}$ ) and the corresponding obtained water levels in the calibration standards ( $m_{H_2O}$ ) for both the instruments.

**Tab. 1** Nominal masses of the CRM HYDRANAL®-Water Standard KF-Oven 220-230 °C to be weighted ( $m_{CRM}$ ) and the corresponding obtained water levels in the three calibration standards ( $m_{H_2O}$ ) for the calibration of the cKF and EWV analysers

	Cal. Std. 1		Cal. Std. 2		Cal. Std. 3	
	$m_{CRM}$ /mg	$m_{H_2O}$ / $\mu$ g	$m_{CRM}$ /mg	$m_{H_2O}$ / $\mu$ g	$m_{CRM}$ /mg	$m_{H_2O}$ / $\mu$ g
<b>cKF</b>	27	1500	36	2000	45	2500
<b>EWV</b>	7.2	400	9	500	10.8	600

The two calibration curves, and their associated analysis curves, were processed with the Weighted Total Least-Squares (WTLS) regression method by exploiting Calibration Curves Computing - CCC Software, a data analysis software developed at INRiM as deliverable of the EMRP project NEW04 “Novel mathematical and statistical approaches to uncertainty

evaluation” [13]. WTLS method takes into account the uncertainties related both to the instrument readings and to the calibration standards.

Aliquots of the sample, to be analysed in single runs, were obtained by cutting the shopping bags in sheets of different size. For cKF, simple sheets having mass of about 80 mg were prepared; for EWV, due to the small dimension of the sample holders, samples were formed by 5 small sheets having mass of about 5 mg each thus leading to a sample mass of around 25 mg for each analytical run. The samples were manipulated by tweezers to avoid the risk of contamination.

The percent water content,  $\%C_i$ , in each sample of Mater-Bi® was determined by using the following model equation:

$$\%C_i = [(a \cdot x_i) / w_i] \cdot 100 \quad (2)$$

Where:

$a$  is the slope of the analysis curve calculated by means of the above mentioned CCC software;

$x_i$  is the instrumental reading for each  $i^{\text{th}}$  sample of biopolymer expressed in mg of water;

$w_i$  is the mass of each  $i^{\text{th}}$  sample of biopolymer expressed in mg of wet mass.

### 3.3 Uncertainty evaluation

The uncertainty associated with each determination was evaluated according to the “Guide to the expression of Uncertainty in Measurement” for both analytical procedures [14, Section 5]. The major uncertainty sources that were considered and individually evaluated are shown in the Ishikawa diagram in figure 1. The diagram highlights the uncertainty contributions for each input quantity,  $a$ ,  $x_i$  and  $w_i$ , in the model equation 2.

In details, the standard uncertainty of the parameter  $a$ ,  $u(a)$ , was obtained by means of the CCC software, which was used to combine the uncertainties related to the calibration standards: on one hand, the repeatability of the measurements of the calibration standards  $x_{\text{CRM}_i}$ , and on the other hand the uncertainties of the nominal values of the calibration standards,  $y_{\text{CRM}_i}$ , which depend on the weighing of each CRM aliquot used as calibration standard ( $m_{\text{CRM}_i}$ ) and on the certified concentration of the CRM,  $c$ .

The standard uncertainty of  $x_i$ ,  $u(x_i)$ , was calculated as the standard deviation of the repeated measurements of the unknown biopolymer aliquots, to take into account the instrumental repeatability in the analytical step.

Finally, the standard uncertainty of  $w_i$ ,  $u(w_i)$ , was evaluated taking into account the uncertainty of the weighing process. The main contributions in this step, which is analogous to the weighing of the calibration standards, come from the repeatability of the balance, the uncertainty of the calibrated masses used as reference and from a correction for the buoyancy effect.

**Fig. 1** Ishikawa diagram for the uncertainty sources of water content ( $\%C_i$ ) in samples of Mater-Bi®

Tables 2 and 3 report an example of uncertainty budget for a measurement carried out by cKF and EWV, respectively.

**Tab. 2** Example of uncertainty budget for a cKF measurement result of  $\%C_i$ .  $U$  is the associated expanded uncertainty ( $k=2$ ).

Input quantity	Uncertainty component	Uncertainty source	Input quantity value	Standard uncertainty value	Relative uncertainty
$x_i$	$u(x_i)$	Instrument repeatability	1.624 mg	$4.5 \cdot 10^{-2}$ mg	$2.8 \cdot 10^{-2}$
$w_i$	$u(w_i)$	Weighing uncertainty	80.63 mg	$5 \cdot 10^{-3}$ mg	$6.2 \cdot 10^{-5}$
$a$	$u(a)$	Analysis curve	0.9515	$9.4 \cdot 10^{-3}$	$9.9 \cdot 10^{-3}$
	$\%C_i = 1.92$		$u(\%C_i) = 0.06$		$U(\%C_i) = 0.12$

**Tab. 3** Example of uncertainty budget for an EWV measurement result of  $\%C_i$ .  $U$  is the associated expanded uncertainty ( $k=2$ ).

Input quantity	Uncertainty component	Uncertainty source	Input quantity value	Standard uncertainty value	Relative uncertainty
$x_i$	$u(x_i)$	Instrument repeatability	0.439 mg	$1.8 \cdot 10^{-2}$ mg	$4.1 \cdot 10^{-2}$
$w_i$	$u(w_i)$	Weighing uncertainty	24.952 mg	$1 \cdot 10^{-3}$ mg	$4 \cdot 10^{-5}$
$a$	$u(a)$	Analysis curve	0.983	$1.5 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$
	$\%C_i = 1.76$		$u(\%C_i) = 0.08$		$U(\%C_i) = 0.16$

Figures 2 and 3 report the results of the single measurements obtained by cKF and EWV analysis, respectively, together with the associated expanded uncertainties (for  $k=2$ ).

**Fig. 2** Results of measurements of Mater-Bi<sup>®</sup> samples as obtained by cKF with the associated expanded uncertainties ( $k=2$ )

**Fig. 3** Results of measurements of Mater-Bi<sup>®</sup> samples as obtained by EWV analysis with the associated expanded uncertainties ( $k=2$ )

The results obtained by cKF method show a better homogeneity among the sample aliquots, allowing a very good measurement repeatability.

The water content estimates in the Mater-Bi<sup>®</sup> sample, as obtained with the two methods, were calculated as the weighted mean of the single results. The uncertainty associated with the values were calculated taking into account the uncertainty of the weighted mean and the measurement repeatability.

Figure 4 shows a comparison between the results obtained both methods with their associated expanded uncertainties ( $k=2$ ).

**Fig. 4** Comparison between the mean water content results obtained by cKF (◆) and EWV (■) methods with the associated expanded uncertainties ( $k=2$ )

The measurement results are in agreement and consistent within the stated uncertainties. The smaller uncertainty associated with the cKF determination is due to a better reproducibility of the single measurements, being the sub-samples more homogeneous (a single sheet, instead of 5) and with a larger mass, hence with a water content that falls inside the best measurement range of the instrument. The fragmentation of the sub-samples for the EWV measurements, which implies the stratification of the single sheets in the sample holder, might lead to an incomplete extraction of the water, hence it may explain the lower value of water content obtained.

#### 4. Conclusions

The present work reports the results obtained by the application of metrologically traceable procedures to the determination of the water content in a sample of Mater-Bi<sup>®</sup> by two coulometric methods, i.e. the cKF titration and the EWV analysis. The novelty of the presented work is due to the exploitation of two techniques selective for water, which allow the determination of the water content avoiding interferences from other volatiles, with great advantages with respect to the Loss on Drying methods.

In addition the developed procedures guarantee the establishment of metrological traceability to the SI of the measurement results.

Metrological traceability of measurement results was established by using appropriate reference materials for the instrument calibrations and calibrated mass standards for determining the masses of the calibration standards and of the sub-samples.

The results obtained with the two techniques are comparable within the stated uncertainties. As expected, the sample manipulation affects significantly the measurement results.

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