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Certification of Standard Reference Material® 2890a Water in 1-Octanol

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Abstract

Standard Reference Material (SRM) 2890a Water in 1-Octanol is intended for use in validating methods and calibrating instruments for the measurement of trace concentration levels of water. SRM 2890a is a solution of water in 1-octanol which is certified for its water content. A unit of SRM 2890a consists of five 5 mL ampoules, each containing approximately 2 mL of water in 1-octanol. This publication documents the production, analytical methods, and computations involved in characterizing this product.

Keywords

Gas Chromatography-Flame Ionization Detection (GC-FID); Karl Fischer (KF) Titration; Mass Balance; Standard Reference Material (SRM); Water Saturated Octanol (WSO).

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1. Introduction

Accurate knowledge of the amount of water in a material can be of great economic importance. The value of crude oil is affected by its water content. Very small amounts of water in transformer oil can cause transformers to short circuit. Water content influences the quality and shelf-life of many pharmaceuticals and food products.

The accurate measurement of water depends on the accurate calibration of measurement systems used for its analysis. Water in 1-octanol standards are widely used for water as measured by Karl Fischer titration. Water in 1-octanol is a low toxicity, stable, non-hygroscopic material with a water content that is effectively independent of temperature from (2 to 30) °C [1].

The National Institute of Standards and Technology (NIST) Standard Reference Material® (SRM®) 2890a Water in 1-Octanol is intended to support trace water measurements in the United States and globally. SRM 2890a is the second member of the SRM 2890 series. The original SRM 2890 Water Saturated 1-Octanol (WSO) [2] became available for purchase in August 1998. The sales history of SRM 2890 is displayed in Fig. 1 as a function of calendar year. The proportions of sales to customers in the US, Europe, Asia, and the rest of the world are displayed in Fig. 2, also as functions of calendar year.

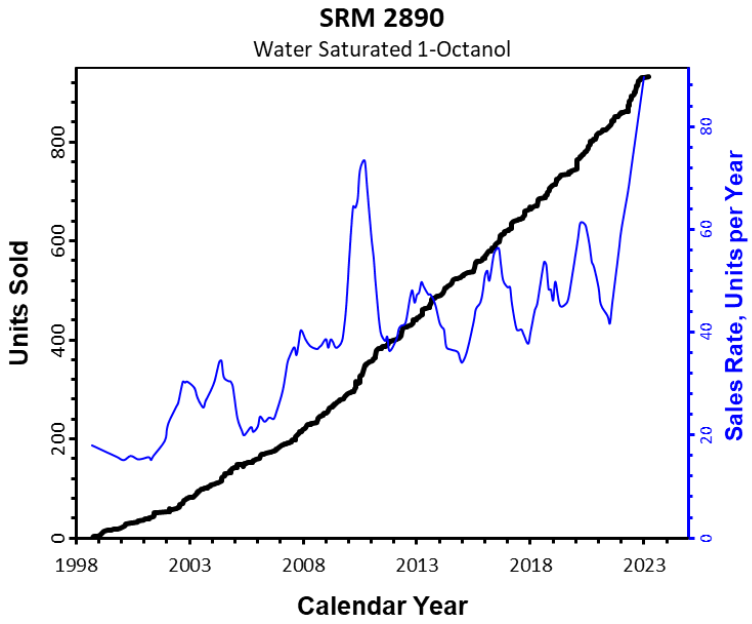


Fig. 1. Sales History of SRM 2890.

The thick black line depicts the cumulative distribution of sales as a function of the order date; it is plotted using the "Units Sold" axis at the left of the plot. The thin blue line depicts the total units sold per year; it is plotted using the "Sales Rate, Units per Year" axis to the right of the graph.

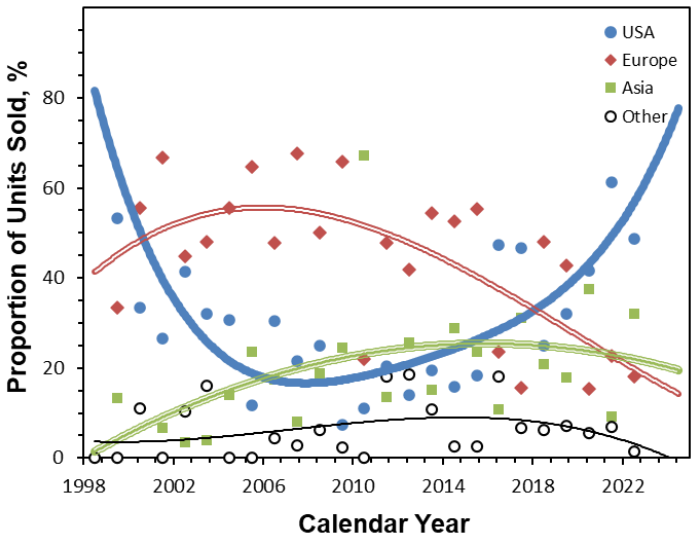


Fig. 2. Location of Customers for SRM 2890.

The solid circles and the thick trendline display the proportion of sales to customers within the USA. Solid diamonds and the double-line trendline display the proportion of units sold to customers in Europe (including the United Kingdom); solid squares and the triple-line trendline display the proportion solid to customers in Asia. The open circles and thin single-line trendline display the proportion of units sold to customers elsewhere.

A unit of SRM 2890a consists of five 5 mL ampoules, each containing approximately 2 mL of water in 1-octanol. The water content of the SRM 2890a material has been assigned using coulometric, volumetric Karl Fischer (KF) titration [3,4,5], and by gas chromatographic determination of the 1-octanol content.

2. Materials and Production

2.1. Materials

Six 2 L bottles of HPLC grade 1-octanol (Sigma) were obtained for the preparation of SRM 2890a.

Ultra-high-purity water was prepared in-house by sub-boiling distillation using a conditioned, quartz still with deionized water as feedstock. This ultra-high purity water has been compared to ASTM Type I water generated on site using Ion Chromatography (IC). The comparison showed that the ultra-high purity water was equivalent in purity or better based on the relative peak areas of the observable anions and cations.

2.2. Solution Preparation.

Twelve liters of the HPLC grade 1-octanol were added to a glass 20 L bottle that had been previously cleaned with water and baked in an oven at 500 °C for 8 hours to remove any organic residue. Approximately 500 mL of ultra-high-purity water was added to the 1-octanol. The solution was covered, and a magnetic stirrer was used to mix the liquids to help the water be absorbed into the 1-octanol. After three days, stirring was stopped and the aqueous phase was allowed to settle for 6 hours. A clean 3.175 mm Polytetrafluoroethylene (PTFE) tube was inserted to the bottom of the bottle and the majority of the aqueous phase was removed, leaving less than 20 mL (approximate) of the free water in the solution bottle. The solution was allowed to resume mixing overnight before the bottle was moved to NIST's Office of Reference Materials (ORM) sample preparation facility in preparation for ampouling.

Once the bottle was delivered to ORM, the bottle was placed back on a magnetic stirrer and the solution headspace of the bottle was allowed to equilibrate with a smaller bottle of a two phase (saturated) system of water and octanol that was attached to a 25 L polyvinyl fluoride bag filled with dry nitrogen gas. This arrangement ensured that the headspace of the SRM solution would not change as the volume of solution in the bottle decreased over the course of ampouling. The SRM solution was allowed to stir and equilibrate at ORM for one day. The night before ampouling, stirring of the SRM bottle was stopped to allow any suspended water droplets in the solution to settle to the bottom of the container.

Prior to ampouling the solution, the supply line for the ampouling machine was set approximately 5 cm from the bottom of the bottle to prevent uptake of any water droplets from the bottom of the container. The ampoules were stored in a total of 32 boxes at ORM, each container numbered in sequence of production order.

3. Density

Density values are required to enable conversion of values from mass fraction basis (w_{H2O} in mg/g) to mass concentration basis (x_{H2O} in mg/mL). Density determinations were made using the Lang-Levy pipette method described in [6] and an Anton Paar DMA 5000 M vibrating tube densimeter.

3.1. Materials

Ten ampoules of SRM 2890a from across the 32 boxes were selected for analysis. High-purity air saturated water (hereafter called water) was the primary control for both methods. SRM 2890 was used as a quasi-control for the Lang-Levy method since the density stated in its Certificate of Analysis [2] is non-certified. The density of air was used as a control for the Anton Paar DMA 5000.

3.2. Methods

3.2.1. Lang-Levy Pipette

Prior to measurements, a 500 µL Lang-Levy pipet, ampoules from boxes 1, 14, 21, and 32 of SRM 2890a, two ampoules of SRM 2890, and water were allowed to equilibrate for at least 16 hours at ambient (19.67 °C to 19.81 °C) balance room temperature. The metal pipette stand was tared on an analytical balance, followed by gentle placement of the clean and dry pipette on the metal stand. The mass of the pipette was recorded. The pipette was then filled to the mark with water, wiped with a lint-free cloth, and weighed in triplicate to obtain an average mass. To clean and dry the pipette, the pipette was attached to a vacuum trap and several mL of water were pulled through the pipette followed by several mL of ethanol. The pipette remained attached to the vacuum trap and air was pulled through the pipette for 10 minutes to ensure it was dried. The water weighing was performed four times. The volume of the pipette was calculated from the weight of water and the density of water at average room temperature of 19.58 °C.

For each ampoule, two sample portions were removed for density analysis. As in the density calibration, the pipette was filled to the mark with the test sample, wiped with a lint-free cloth, and weighed in triplicate to obtain an average mass. The pipette was cleaned by attaching the pipette to a vacuum trap and several mL of ethanol were pulled through the pipette and allowed to dry as above. The weighing procedure was repeated for the SRM 2890a test portions and SRM 2890 control portions. Between each measurement, the pipette was rinsed with ethanol and dried for 10 minutes under vacuum. The temperature was recorded between each ampoule measurement.

3.2.2. Anton Paar DMA 5000 M

The Anton Paar DMA 5000 M density meter has a resolution of 0.000 001 g/mL for density and of 0.001 °C for temperature. These resolutions are more than adequate for the uncertainty of the density determinations required for this analysis. The instrument is a vibrating tube densimeter and uses the periodic frequency of the U-shaped tube filled with the solution of interest to determine the density. For initial and final measurements of air density and water density, the meter was set to provide values in its highest accuracy mode at 20 °C. Density measurements of were made at 20 °C, 22 °C, and 25 °C.

Ampoules measured by the DMA 5000 were from boxes 1, 8, 12, 22, 25, and 31. Density was determined using the following general pattern: air and then water at all three temperatures, followed by a test portion of either SRM 2890a or SRM 2890, with the test portion being measured at all three temperatures. After the experiment was concluded for a day, a measurement of water was made again at all three temperatures. Density measurements on the DMA 5000 density meter were made on two different days, with the same general procedure each day.

3.3. Results

The balance room temperature was monitored during the Lang-Levy pipette measurements. The mean calculated volume of the nominal 500 µL pipet at the beginning of measurements was (508.51 ± 0.19) µL and (508.38 ± 0.11) µL at the end. Since the measurement variation was small (< 0.03 %) and water temperature fluctuates less than air temperature, the average (508.41 ± 0.16) µL volume of the pipette was used for all measurements. The Lang-Levy density measurements for the SRM materials are given in Table 1.

Table 1. Lang-Levy Pipette Method Density Estimates for SRMs 2890 and 2890a.

		Temperature, °C		Mass, g	Density, g/mL		
SRM	Box	T	$\bar{T}$ [a]	m_{SRM}	ρ_{SRM}	$\bar{\rho}_{\mathrm{SRM}}$ [a]	$s(\rho_{\mathrm{SRM}})$ [b]
2890a	14	19.56	19.66	0.42283	0.83167	0.83206	0.00021
	14	19.56		0.42306	0.83212		
	21	19.70		0.42309	0.83218		
	21	19.70		0.42305	0.83210		
	1	19.66		0.42312	0.83224		
	1	19.66		0.42308	0.83216		
	32	19.70		0.42288	0.83177		
	32	19.70		0.42310	0.83220		
2890		19.70	19.70	0.42310	0.83220	0.83200	0.00022
		19.70		0.42301	0.83203		
		19.70		0.42288	0.83177		

a Mean of measured values

b Standard deviation of measured values

The density measurements of water and air made using the DMA 5000 were in good agreement with internationally recognized literature reference values [7,8], differing by no more than 0.00002 g/mL for any given measurement. This agreement demonstrated that the instrument was in good working order. The DMA 5000 density measurements for the SRM materials are given in Table 2.

Table 2. Anton Paar DMA 5000 Density Estimates for SRMs 2890 and 2890a.

		Temperature, °C		Density, g/mL		
SRM	Box	T	$\bar{T}$ [a]	ρ_{SRM}	$\bar{\rho}_{SRM}$ [a]	$s(\rho_{SRM})$ [b]
2890a	22	20.009	20.008	0.83251	0.83250	0.00001
	1	20.006		0.83251		
	31	20.005		0.83250		
	8	20.008		0.83249		
	12	20.010		0.83250		
	22	21.990	22.001	0.83111	0.83110	0.00001
	1	22.006		0.83110		
	31	21.991		0.83110		
	8	22.008		0.83108		
	25	22.009		0.83109		
	12	21.995		0.83110		
	22	24.991	24.993	0.82898	0.82897	0.00001
	1	24.991		0.82898		
	31	24.991		0.82897		
	8	24.996		0.82896		
	25	24.995		0.82897		
	12	25.002		0.82896		
2890		20.009	20.010	0.83241	0.83240	0.00002
		20.010		0.83238		
		22.009	22.009	0.83099	0.83098	0.00002
		22.009		0.83096		
		24.994	25.000	0.82888	0.82886	0.00003
		25.006		0.82884		

a Mean of measured values

b Standard deviation of measured values

The density measurements using both methods are displayed in Fig. 4, along with the non-certified value for SRM 2890 listed in its Certificate of Analysis (COA) [2]. The figure displays a theoretical density for the SRMs as a function of temperature based on the known densities of water and octanol, the approximate water mass fraction, and the calculated excess molar volume of mixing the two liquids [1]. While within each method the results for SRM 2890 and 2890a are very similar, those from the Lang-Levy pipette method are somewhat lower than expected from both the trend in the DMA 5000 measurements and theory.

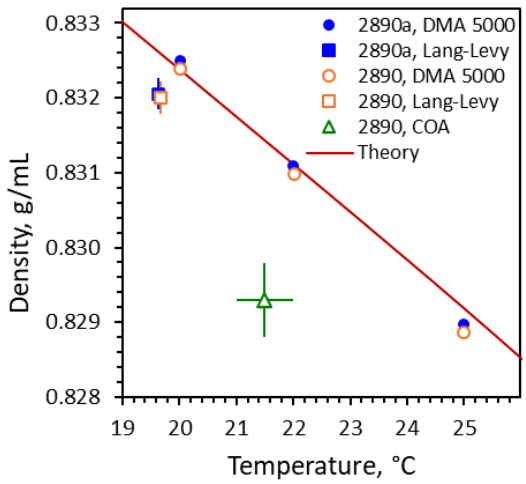


Fig. 3. Density Measurements for SRMs 2890 and 2890a.

Solid symbols denote the mean density estimates for SRM 2890a; open symbols denote estimates for SRM 3890. Circles denote Anton Paar DMA 5000 results; squares denote results provided by the Lang-Levey pipette method; and the triangle represents the non-certified density listed in the SRM 2890 Certificate of Analysis (COA). Vertical error bars represent standard deviations. The horizontal bar of the SRM 2890 COA value spans the stated 1 °C reference range.

The non-certified density of SRM 2890 from the COA is much less than the current measurements. Unfortunately, details of the measurement process used in 1997/8 to provide the result are unavailable. Based on the agreement between the current Lang-Levy and DMA 5000 measurements and the theory-driven function, the value listed in the SRM 2890 COA may be biased low by about 0.002 g/mL.

For the non-certified density of SRM 2890a, the combined uncertainty, u_c, is estimated by adding in quadrature the precision of the results (standard deviation), deviations from theoretical density of the water measurements (0.00001 g/mL), and hypothetical variations in the density based on the uncertainty of the water mass fraction in SRM 2890a. Using a coverage factor of $k = 2.571$ (for $n = 6$) an estimate of the expanded uncertainty, U, at the 95 percent confidence interval is calculated as $U = k \cdot u_c$. The resultant densities with the estimated uncertainties of SRM 2890a at various temperatures are: 20 °C, ρ_{20} = (0.83250 ± 0.00025) g/mL; 22 °C, ρ_{22} = (0.83110 ± 0.00025) g/mL; and 25 °C, ρ_{25} = (0.82897 ± 0.00026) g/mL.

4. Karl Fischer Measurements

4.1. Sampling

Three ampoules from the first and last boxes plus two ampoules each of an additional 22 boxes were taken for analytical measurements for the value assignment of the SRM. Assuming that box number indicates the boxing sequence in time, it is best to spread sampling as uniformly as possible throughout the 32 boxes. Under this assumption, the boxes were selected so that when their integer identifiers are ordered, the largest gap between identifiers is 2. Connecting to the minimax principle in decision theory, the maximum gap between box identifiers was minimized. One ampoule from each chosen box was used in the coulometric Karl Fischer measurements. A smaller subset of the ampoules was set aside for volumetric Karl Fischer measurements.

4.2. Materials

A new 1 L bottle of anhydrous 1-octanol and a new 1 L bottle of anhydrous 1-hexanol were obtained from Sigma-Aldrich. The bottles of 1-octanol and 1-hexanol were equipped with sure seal caps and septa, so that portions could be removed without exposing the bulk of the liquid to moisture in the atmosphere. A bottle of a different batch of anhydrous 1-octanol previously obtained from Sigma-Aldrich was also used.

Ultra-high-purity water (described above) was used in the preparation of standard solutions. Based on ion chromatography measurement of the ultra-high-purity water, the only observed impurity is carbon dioxide (measurable as carbonate). The dissolved carbon dioxide mass fraction, w_{CO2}, was estimated by first assuming an atmospheric carbon dioxide mole fraction, x_{CO2}, of 1800 µmol/mol to account for indoor CO_2 levels (outside x_{CO2} levels are ≈420 µmol/mol [9]). Henry's Law was used to calculate maximum value of w_{CO2} based on the atmospheric concentrations of 3.1×10^{-6} g/g. The working value of w_{CO2} is one-half of this the maximum with an estimated uncertainty as one-half the maximum with a uniform distribution [10], giving, $w_{CO2} = (1.6 \pm 0.9) \times 10^{-6}$ g/g. The overall purity of the water is estimated as (0.999984 ± 0.000009) g/g.

The reagent used in the coulometric Karl Fischer system was Hydranal Coulomat AG (Honeywell/Fluka). The reagents used in the volumetric Karl Fischer system were Hydranal composite 2 (Honeywell/Fluka) and HPLC grade methanol (Fisher).

4.3. Calibration Solutions.

A series of calibration solutions were made by gravimetrically adding water into anhydrous 1-octanol. The new bottles of anhydrous 1-octanol and anhydrous 1-hexanol were used to prepare the calibration solutions. The octanol and water were weighed out on an analytical balance into 6 mL auto-sampler vials that contained a micro stir bar. The anhydrous alcohols were transferred from their original bottles to the autosampler vials using a 5 mL gas tight syringe to minimize water uptake. After weighing, the vials were crimp sealed with a PTFE/butyl rubber septum. The vials were then placed on a magnetic stirrer to aid solvation of the water

into the alcohols. This is especially critical for the solutions that are close to saturation. The vials were allowed to stand for a few days to ensure complete dissolution of the water since some micelle formation is possible. The vials were weighed again after sealing and prior to the calibration measurements on the Karl Fischer system to confirm that the vials were sealed and minimal mass exchange between the sample and the environment had taken place. The water content was determined as a mass fraction based on water added to the vial plus the small fraction of water present in the 1-octanol (0.06 mg/g). Table 3 lists the water mass fractions, w_{H2O}, in the calibration solutions used in the coulometric and volumetric KF water measurements.

Table 3. Calibration Solutions used in the Karl Fischer Measurements of SRM 2890a.

Coulometric KF Calibrants, mg/g

Calibrant	Solvent	w_{H2O}	$u(w_{H2O})$
D	1-octanol	27.466	0.016
F	1-octanol	31.320	0.017
K	1-octanol	37.049	0.016
M	1-octanol	37.587	0.016
R	1-octanol	41.771	0.016
V	1-octanol	43.354	0.016
X	1-octanol	43.771	0.017
B1	1-hexanol	38.006	0.016
E1	1-hexanol	41.622	0.016
I1	1-hexanol	40.745	0.016
J1	1-hexanol	42.577	0.016
K1	1-hexanol	51.758	0.016

Volumetric KF Calibrants, mg/g

Calibrant	Solvent	w_{H2O}	$u(w_{H2O})$
D2	1-hexanol	45.650	0.015
E2	1-hexanol	46.001	0.015
G2	1-hexanol	46.941	0.015
H2	1-hexanol	48.921	0.015
M2	1-hexanol	51.700	0.015
N2	1-hexanol	52.558	0.015
Q2	1-hexanol	54.202	0.015
R2	1-hexanol	54.859	0.015

The standard uncertainties of the water mass fractions ($u(w_{H2O})$) in the calibrants were calculated using a propagation of errors methods that included the uncertainty of the weighing, uncertainty of the purity of the ultra-high-purity water, and the uncertainty of the water in the solvent [11,12].

4.4. Solvent Blanks

Blanks of the 1-octanol and 1-hexanol solvents were prepared as in section 4.3 to help account for water pickup from the atmosphere and the autosampler bottles.

4.5. Controls

SRM 2890 Water saturated 1-Octanol was used as a control sample. A secondary control of water saturated octanol (WSO2) was used to help determine daily variations of measurements on the coulometric Karl Fisher system in support of the SRM 2890a homogeneity assessment.

The WSO2 was prepared by mixing approximately 100 mL of the second bottle of anhydrous 1-octanol with excess ultra-high-purity water. This was placed for several days on a mechanical shaker and also stirred to saturate the 1-octanol with water. Water is left at the bottom of the container to ensure that the system is always at equilibrium as a two-phase system, where the

organic phase is used for water measurements. The WSO2 as prepared was stored on the benchtop. Previous WSO solutions made and stored in a similar manner have been found stable with respect to water mass fraction for several years [1].

4.6. Sample Preparation

For the Karl Fischer analysis, sample test portions of SRM 2890 and SRM 2890a were used “as is” with no preparation. Aliquots of these materials were handled using a gas-tight syringe.

4.7. Weighing

Mass determinations were made using a calibrated 5-place Sartorius MC 210S balance that is serviced and calibrated annually. The calibration was verified using 5 g and 50 g standard masses that are traceable to the SI through the standard mass set maintained by NIST’s Inorganic Chemical Metrology Group. All masses were recorded by hand.

4.8. Coulometric Karl Fischer

One of the three determinations of the water content and a homogeneity analysis of SRM 2890a was made on a coulometric Karl Fischer system. The coulometric Karl Fischer system was set up using a frit-less generator electrode using approximately 200 ml of Hydranal Coulomat AG. The Karl Fischer system was started and allowed to run overnight to fully equilibrate prior to test measurements. On each day of the test measurements, an initial baseline drift was determined by performing a titration with the system with no injections prior to analysis.

The first two days of the analysis were used to calibrate the coulometric Karl Fischer system using the calibrants described in Table 3. Three calibration measurements using 120 mg (nominal) of the calibration standards were made by injecting the standard into the Karl Fischer titration vessel through a silicone septum via a gas-tight syringe. The amount injected into the Karl Fischer cell was determined by weighing the injection syringe before and after the injection. To ensure consistency for each run, all titrations were run for 30 minutes rather than by electrochemical potential of the cell alone.

Following the calibration measurements, water mass fraction measurements of SRM 2890a were made on six days. Over the course of the measurements, test portions of SRM 2890a and SRM 2890 were run in a pre-determined random order. Furthermore, on each day of the measurement a sample of was run to look for daily variations in the coulometric KF measurement.

Test portions of SRM 2890a and SRM 2890 were sampled by breaking the ampoule open and transferring the contents of the ampoule to a clean 5 mL gas-tight syringe with a pressure-lok® valve (rinsing with a small amount of the ampoules contents prior to filling the syringe). Like the calibration samples, the test portions of SRM 2890a, SRM 2890, and were introduced into the Karl Fischer titration cell using a syringe through a silicone septum, and the amount injected determined by weighing the syringe before and after the injection on analytical balance.

For the first three days all titrations were run for 30 minutes for consistency, but for the last three days it was determined that using a pattern of one 30-minute run followed by six 15-minute runs was sufficient to measure the water mass fractions without sacrificing precision. The 30-minute runs were used to ensure the instrument drift did not change significantly over the course of a day. Typical baseline drifts were around 0.50 µg of water per min. The drift corrected Karl Fischer signals were used in the determination of water in SRM 2890a. At the conclusion of the measurements of SRM 2890a by coulometric Karl Fisher, a small set of calibration samples was measured to verify there was no drift in the calibration.

The calculation of the water content by coulometric Karl Fischer have been described elsewhere [3,13,14]. Briefly, the simplest calculation of the water mass fraction, w_{H20}, by coulometric Karl Fischer is to divide the endpoint mass of water from the coulometric instrument, m_{ep} (µg), by the sample mass, m_s (g), whereby $w_{H20} = m_{ep}/m_s$ (mg/g). However, this does not take into account the instrument drift of the system, d, where d is change of mass per unit time (µg/min). The drift correction for a titration of that takes time t in minutes to complete is $d \cdot t$. Thus, the drift corrected mass fraction in mg/g is:

$$\boldsymbol{w_{\mathrm{H2O}} = \frac{m_{ep} - d \cdot t}{1000 \cdot m_s}}. \quad (1)$$

Further refinement to the mass faction will also be made by applying a calibration correction using known calibration standards to account for instrumental variations in the conversion of the assumed reduction of I_2 to I^- to the mass of water. The effective measurement equation for water in SRM 2890a by coulometric Karl Fischer is:

$$\boldsymbol{w_{\mathrm{H2O}} = R \cdot C_{WH} \cdot \left(\frac{m_{ep} - d \cdot t}{1000 \cdot m_s} - a_0 \right) / a_1}, \quad (2)$$

where a_0 and a_1 are the intercept and slope of the calibration curve (respectively), C_{WH}, defined to have a value of unity, is the uncertainty from the calibration curve (incorporation of the C_{WH} term is discussed in section 4.8.5), and R, defined to have a value of unity, is the replication uncertainty.

4.8.1. Calibration

The coulometric KF instrument calibration curve is shown in Panel A of Fig. 4, where the coulometric mass fraction water content of the calibration solutions is plotted as a function of their gravimetric preparation values. The residuals of the calibration curve ($w_{measured}$- w_{fit}) are shown in Panel B of Fig. 4, demonstrating the linear response of the instrument. Also shown in Panel B are three verification measurements of calibration samples run at the end of the measurements and that were not included in the calibration that demonstrate the calibration did not drift significantly over the course of the SRM 2890a analysis.

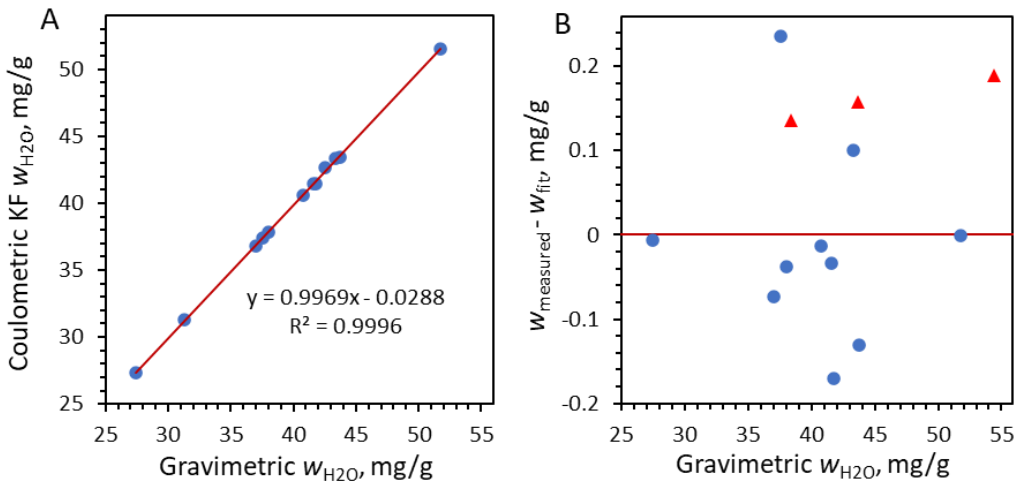


Fig. 4. Calibration Model for Coulometric KF w_{H2O}.

Panel A) Each symbol denotes the {gravimetric, coulometric) mass fraction water estimates for one calibration solution. The line represents the linear calibration model; the inset text displays the calibration equation. Panel B) Each symbol denotes a residual, which is the difference between the coulometric KF mass fraction water measurement ($w_{measured}$) and the value predicted by the calibration model (w_{fit}). The circles (●) denote residuals for the calibration solutions used to parameterize the model. Triangles (▲) denote residuals for three calibration check measurements made at the end of the KF measurements to check for drift.

4.8.2. Mass Fraction Water in SRM 2890a

The measured water mass fraction of the test samples of SRM 2890a by coulometric Karl Fischer is given in Table 4. The table lists the analysis day, the box number from where the sample was pulled, the sample mass of each replicate (m_{2890a}), and the water mass fraction (w_{2890a}).

Table 4. Triplicate Measurements for 24 SRM 2890a Ampoules by Coulometric Karl Fischer Titration.

Day	Box	m_{2890a}, g	w_{2890a}, mg/g	Day	Box	m_{2890a}, g	w_{2890a}, mg/g	Day	Box	m_{2890a}, g	w_{2890a}, mg/g
1	12	0.06309	47.053	4	10	0.06936	47.142	5	3	0.06930	47.021
1	12	0.06005	46.944	4	10	0.06451	47.105	5	3	0.05760	47.177
1	12	0.03829	46.988	4	10	0.04293	47.108	5	3	0.06708	47.121
1	24	0.07740	47.198	4	31	0.06090	46.796	5	29	0.06543	47.203
1	24	0.04662	47.179	4	31	0.08019	46.779	5	29	0.09508	47.135
1	24	0.06596	47.131	4	31	0.05600	46.883	5	29	0.06297	47.310
2	19	0.10723	47.218	4	14	0.05951	47.202	6	5	0.06701	47.216
2	19	0.06572	47.015	4	14	0.05209	47.334	6	5	0.06152	47.063
2	19	0.06422	47.139	4	14	0.07864	47.088	6	5	0.07173	47.044
2	4	0.07531	47.110	4	1	0.07937	47.040	6	17	0.06751	47.212
2	4	0.05875	47.194	4	1	0.05537	47.185	6	17	0.07848	47.201
2	4	0.04559	47.045	4	1	0.07544	47.067	6	17	0.06684	47.249
2	11	0.09448	47.051	4	8	0.07437	47.147	6	29*	0.06113	46.932
2	11	0.04336	47.024	4	8	0.06302	47.244	6	29*	0.07639	47.051
2	11	0.07425	47.056	4	8	0.06751	47.144	6	29*	0.06741	47.161
3	16	0.06480	46.985	5	25	0.09282	47.054	6	23	0.06835	47.197
3	16	0.08060	46.931	5	25	0.05860	47.008	6	23	0.06755	47.266
3	16	0.07887	47.108	5	25	0.06459	47.203	6	23	0.06155	47.209
3	6	0.08692	47.022	5	1*	0.05654	47.125	6	21	0.06437	46.933
3	6	0.08217	46.939	5	1*	0.06175	46.986	6	21	0.07634	47.059
3	6	0.07851	47.147	5	1*	0.07617	47.119	6	21	0.06438	47.046
3	27	0.08147	47.042	5	32	0.05788	47.197	6	22	0.06677	47.218
3	27	0.04999	47.084	5	32	0.06842	47.130	6	22	0.04754	47.054
3	27	0.07350	46.888	5	32	0.06756	47.084	6	22	0.06777	47.114
4	16*	0.07151	47.013	5	18	0.06817	47.167	6	28	0.09839	47.108
4	16*	0.05470	47.094	5	18	0.06161	47.092	6	28	0.04884	47.119
4	16*	0.07563	47.001	5	18	0.05606	47.197	6	28	0.05688	47.130

* Replicates noted here are results from confirmatory measurements made one day after the initial measurements

Table 5 gives the average water mass fraction for each ampoule and its uncertainty, $u(w_{H2O})$. The uncertainty of the ampoule water mass fraction is estimated by propagating uncertainties through Eq. (**2**. A full description of the uncertainty calculation is given in Section 4.8.5.

Table 5. Mean Results for 24 SRM 2890a Ampoules by Coulometric Karl Fischer Titration.

Box	$\overline{w}_{2890a}$, *mg/g*	$u(\overline{w}_{2890a})$, mg/g	Box	$\overline{w}_{2890a}$, *mg/g*	$u(\overline{w}_{2890a})$, mg/g	Box	$\overline{w}_{2890a}$, *mg/g*	$u(\overline{w}_{2890a})$, mg/g
1	47.097	0.081	12	46.995	0.060	23	47.224	0.045
3	47.106	0.083	14	47.208	0.126	24	47.169	0.043
4	47.116	0.079	16	47.008	0.094	25	47.088	0.105
5	47.108	0.098	17	47.221	0.035	27	47.005	0.106
6	47.036	0.108	18	47.152	0.060	28	47.119	0.027
8	47.178	0.062	19	47.124	0.105	29	47.216	0.092
10	47.118	0.032	21	47.013	0.074	31	46.819	0.061
11	47.044	0.030	22	47.129	0.087	32	47.137	0.062

N: 24
Mean: 47.101
Standard Deviation: 0.092

The measured water mass fraction for each ampoule of SRM 2890a is shown in Fig. 5 by the order of analysis (Day order). There is no apparent trend in w_{2890a} across the analysis sequence.

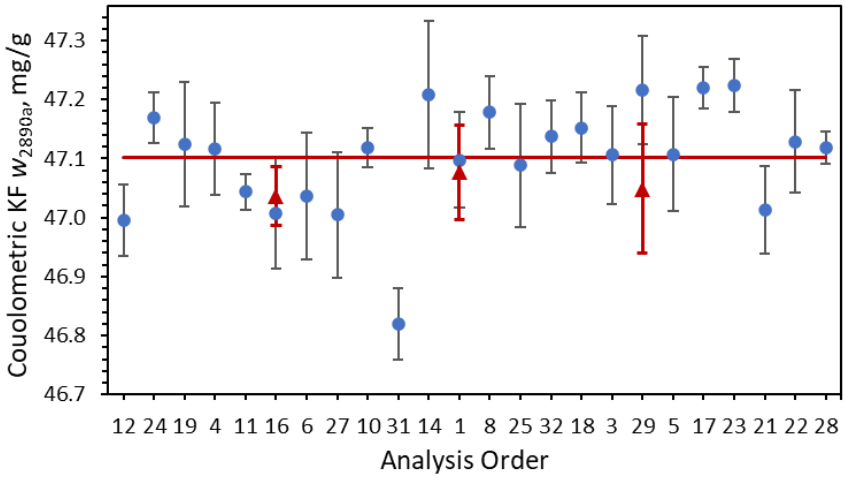


Fig. 5. Coulometric KF w_{2890a} In Order of Ampoule Analysis.

Each symbol represents the mean of three aliquots from one ampoule of SRM 2890a. The circles denote results from initial measurements, triangles denote results from confirmatory measurements made one day after the initial measurements. Error bars represent standard uncertainties. The horizontal line represents the mean of the 24 initial mean values.

Measurements for ampoules from boxes 1, 16, and 29 were repeated on the next day and are also shown in Fig. 5. These duplicate results were made using portions of the ampoules stored overnight in the 5 mL gas-tight syringe used to dispense aliquots of the SRM. They were made to examine the day-to-day variability of the coulometric water determinations. The duplicate w_{2890a} values generally agree well with the primary values, although the sample from box 29 is lower than the original measured value. However, the determined value agrees with the total dataset, as is likely due to water loss on overnight storage.

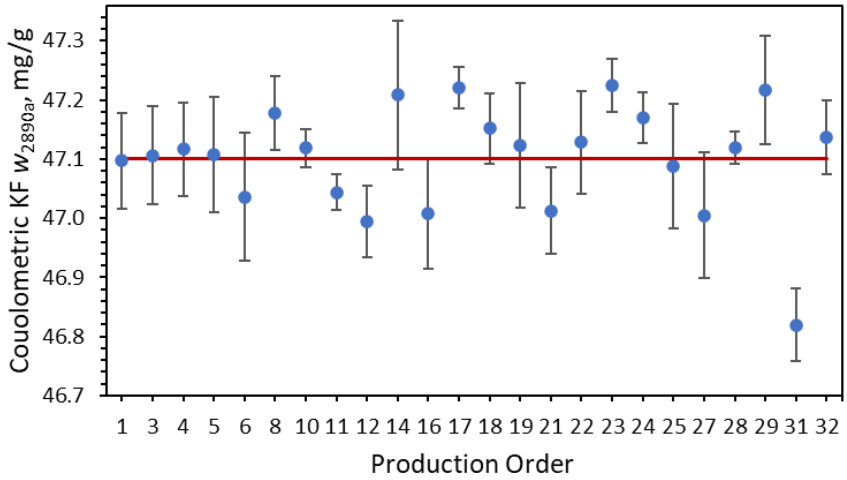


Fig. 6. Coulometric KF w_{2890a} In Order of Ampoule Production.

Each symbol represents the mean of three aliquots from one ampoule of SRM 2890a. Error bars represent standard uncertainties. The horizontal line represents the mean of the 24 mean values.

The w_{2890a} for the SRM 2890a ampoules are shown in Fig. 6 in the order of ampoule production (Box order). There is no apparent trend in w_{2890a} across the production sequence. However, there is statistically significant between-ampoule variance, which can be observed in the ampoule from box 31, suggesting that there may be a degree of heterogeneity in the SRM. Any heterogeneity will ultimately be accounted for in the calculation of the expanded uncertainty.

4.8.3. Mass Fraction Water in WSO2 Control Material

The measured water mass fraction for WSO2 control samples by coulometric Karl Fischer is given in Table 6.

Table 6. Results for WSO2 Control Material by Coulometric Karl Fischer Titration.

Day	m_{WSO2}, g	w_{WSO2}, mg/g	$\overline{w}_{\mathrm{WSO2}}$, mg/g	$s(w_{\mathrm{WSO2}})$, mg/g	$u(\overline{w}_{\mathrm{WSO2}})$, mg/g
1	0.06759	48.928			
1	0.06755	49.029			
1	0.06385	49.495	49.165	0.221	0.223
1	0.04078	49.262			
1	0.04126	49.112			
2	0.03965	49.228			
2	0.04453	48.859	49.027	0.187	0.188
2	0.04454	48.994			
3	0.05456	49.078			
3	0.04698	49.143	49.121	0.037	0.045
3	0.05151	49.141			
4	0.05845	49.205			
4	0.04157	49.364	49.238	0.085	0.088
4	0.05330	49.199			
4	0.04608	49.183			
5	0.04057	49.309			
5	0.06856	49.065			
5	0.06928	49.152	49.157	0.091	0.094
5	0.05002	49.124			
5	0.06772	49.135			
6	0.04760	49.161			
6	0.04508	49.292	49.220	0.096	0.099
6	0.03684	49.117			
6	0.04282	49.310			
		N:	6		
		Mean:	49.115		
		Standard Deviation:	0.076		

The daily measured water mass fraction of the WSO2 control material (w_{WSO2}) is shown in Fig. 7. The daily measurements are in good agreement with no obvious trend over time.

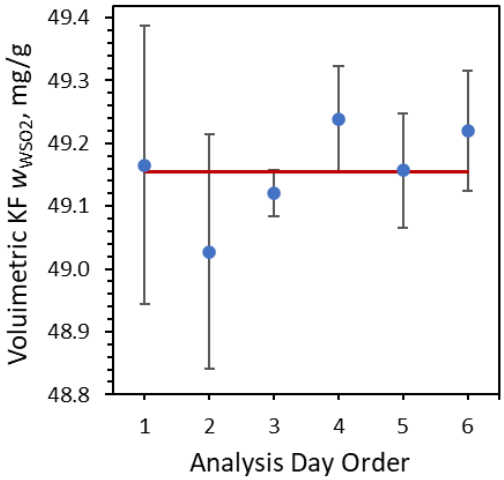


Fig. 7. Daily Coulometric Measurements of the WSO2 Daily Control Material.

Each symbol represents the mean of three to five aliquots of the WSO2 daily control material. Error bars represent standard uncertainties. The horizontal line represents the mean of the six mean values.

4.8.4. Mass Fraction Water in SRM 2890 Control Material

Table 7 lists the water mass fraction results for the SRM 2890 Control. These results are compared to the SRM 2890 certified value and stability measurements made in 2008 and 2015 in Fig. 8.

Table 7. Results for SRM 2890 Control Material by Coulometric Karl Fischer Titration.

Day	m_{2890}, g	w_{2890}, mg/g	$\bar{w}_{2890}$, mg/g	$s(w_{2890})$, mg/g	$u(w_{2890})$, mg/g
1	0.06729	48.174			
1	0.05771	48.207	48.171	0.038	0.046
1	0.07997	48.131			
4	0.05809	48.228			
4	0.07771	48.047	48.090	0.126	0.130
4	0.05482	47.986			
5	0.07303	48.100			
5	0.06612	48.240	48.140	0.088	0.091
5	0.07935	48.078			
		N	3		
		Mean	48.134		
		Standard Deviation:	0.041		

While the current results are within the SRM 2890 certified uncertainty interval [2], measurements made after the original 1998 certification are quite uniformly biased high relative to the certified value. This bias is likely due to SRM 2890 having been certified using volumetric additions to the Karl Fischer cell rather than the current practice of gravimetric additions. The mass concentration values resulting from these measurements were converted

to mass fraction using a poorly documented value for the density of the material, which is likely the source of the bias in the determined mass fractions of SRM 2890.

The water mass fraction of SRM 2890 has been consistent for 16 years, suggesting that SRM 2890a will have a shelf life of at least 20 years.

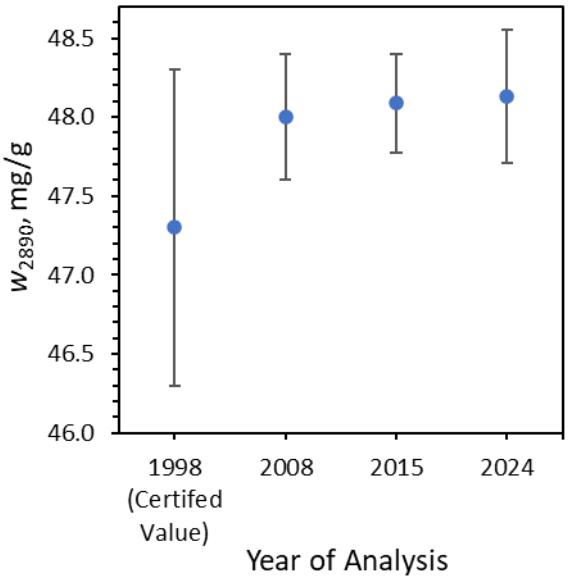


Fig. 8. Water Mass Fraction of SRM 2890 Over Time.

Each symbol represents an estimate of the mass fraction water in SRM 2680. The 1998 value is the certified mass fraction. The 2008 and 2015 values are from routine stability confirmation studies. The 2024 value is from the current study. Error bars represent approximate 95 % level of confidence expanded uncertainties, however for the stability analysis, the uncertainties cover only the NIST KF measurements but not other potential sources of error.

4.8.5. Uncertainty Components

Uncertainty estimates for each component of the coulometric Karl Fischer method are listed in Table 8. The components of uncertainty can be used to estimate the uncertainty for each individual measurement of SRM 2890a and for the control samples of SRM 2890.

Table 8. Components of uncertainty in the coulometric Karl Fischer measurements.

Measurement	Value	Type [a]	Distribution	range	uncertainty
mass (m_s)	0.04 g	B	Rectangular	± 0.03 mg [b]	0.017 mg
titration time (t)	30-15 min	B	Normal	± 1 s [c]	0.5 se
nominal water (m_{ep})	< 1000 µg	B	Rectangular	± 3 µg [b]	1.732 µg
	> 1000 µg	B	Rectangular	± 0.3 % [b]	0.17%
drift rate (d)	0.4 µg/min	B	Rectangular	± 0.05 µg/min [c]	0.03 µg/min
intercept (a_0)	0.9969		-	0 [d]	0
slope (a_0)	0.0288		-	0 [d]	0
Calibration (C_{WH})	1	A	Rectangular	± 0.00365 [e]	0.00245
replication (R)	1	A	Normal	± 0.0015	0.0011

a A or B identifies whether a Type A or B approach is used to evaluate the standard uncertainty component.
b Values given for the ranges are from the manufacturer. Distributions are assigned by the authors.
c Values given for the ranges are from multiple observations of instrument performance during operations.

d Uncertainty for the slope and intercept folded into the calibration term, C_{WH}, using the working-Hotelling method, thus are set to zero to avoid double counting. The Working-Hotelling method is preferred because the confidence interval using this method is thought to be a better predictor of the uncertainty.

e Calculated using the Working Hotelling method.

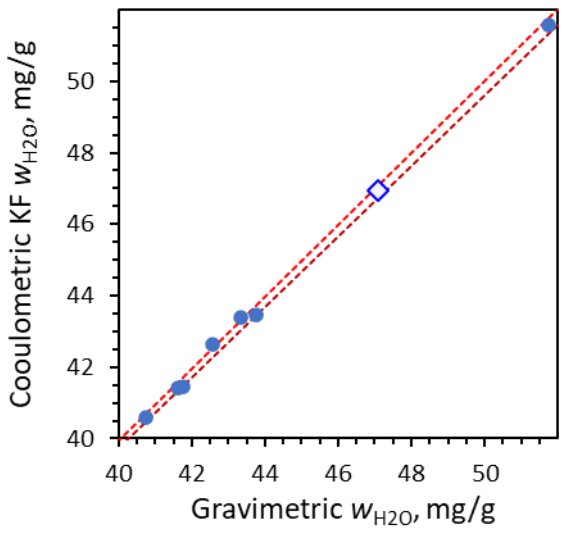


Fig. 9. Calibration Curve for the Coulometric KF Measurements.

The calibration curve for the coulometric Karl Fisher measurements with the measured value of SRM 2890a shown, ♦. Shown is the select calibration standards, ●, the calibration curve, ——, and the upper and lower 95 % confidence bands of Working-Hotelling model, – – –. The error bars for SRM 2890a are the estimated uncertainty, u_H from the confidence bands of Working-Hotelling confidence bands as projected along the x-axis.

One of the uncertainty components that was briefly touched on in Sec. 4.8 comes from the calibration curve. Uncertainty for the measurements at the 95 percent confidence interval was estimated using Working-Hotelling confidence bands [15]. The Working-Hotelling method is preferred over using the uncertainties of the slope and intercept (calculated for linear regression) because the confidence interval is based on where the test value is in relation to the mean value of the calibration curve and is thought to be a better predictor of the uncertainty. Figure Fig. 9 shows the measured mass fraction of candidate SRM 2890a with the uncertainty from the Working-Hotelling confidence bands. The intersection of the confidence bands with the water mass fraction of candidate SRM 2890a from the Karl Fischer response (y-axis) was used to project the confidence interval onto the expected value (x-axis). For the 47.10 mg/g water mass fraction of candidate SRM 2890a, the 95 percent confidence interval of the Working-Hotelling model is ± 0.168 mg/g. For inclusion in Eq. 2, since the uncertainty from the calibration curve, C_{WH}, is defined to have a value of unity, the confidence interval is normalized by dividing by w_{H20} to give 0.00356. Assuming a rectangular distribution, the uncertainty for the calibration curve is, $u(C_{WH})$= 0.00245. Note that the uncertainty components for the slope and intercept of the calibration curve (a_1 and a_0, respectively) are set to zero to avoid double counting since this uncertainty is calculated as C_{WH}

The uncertainty estimate for each ampoule is calculated using the Guide to the Expression of Uncertainty in Measurement (GUM) to propagate errors using Eq. 2 [11,12,16]. These values are given in Table 5.

The combined standard uncertainty for the coulometric Karl Fischer measurements of SRM 2890 control is calculated in the same manner, and the resultant uncertainty is u_c = 0.097 mg/g. Using a coverage factor of k = 4.302 (for n = 3) the expanded uncertainty, U, at the 95 percent confidence interval is U = 0.42 mg/g, where $U = k \cdot u_c$. This value is discussed in section 4.8.4 and shown in Fig. 8.

4.9. Volumetric Karl Fischer

The water content of SRM 2890a was also made on a volumetric Karl Fischer system with Hydranal composite 2 as the Karl Fischer reagent and anhydrous methanol as the solvent. The day before each measurement, approximately 80 mL of methanol was added to the Karl Fischer vessel and the Karl Fischer system was run overnight to fully equilibrate.

On the day of the test measurements, the titer or factor (mg of water per volume of solution delivered) of the Hydranal composite 2 solution was determined from three injections of a calibration standard (see Table 3). As with the coulometric measurements, the amount of calibration standard injected into the Karl Fischer cell was determined by weighing the injection syringe before and after the injection on an analytical balance.

Following the calibration measurements, test portions of SRM 2890a or SRM 2890 were measured on the volumetric Karl Fischer system. The test portions for the volumetric titration were handled in the same manner as the coulometric KF measurements.

All titrations were run for a set length of time (30 minutes) rather than a duration determined by the electrochemical potential of the cell alone. The drift of the instrument was calculated at the conclusion of every run over two successive 10-minute intervals to check for consistency in the baseline and to calculate the adjusted Karl Fischer signal due to system drift. Typical drifts for the volumetric Karl Fisher titrator were between 1 µL and 2 µL of composite 2 solution per minute.

The calculation of the water content by Karl Fischer methods is described elsewhere [3,13,14]. Briefly, the simplest method for calculating the water mass fraction, w_{H20}, by volumetric Karl Fischer titration is determined by dividing the volume of the Hydranal composite 2 titrated into the Karl Fischer cell (in mL), v_{KF}, is divided by the sample mass, m_s, and then multiplied by the titer (or factor as µg water per mL of solution) of the Hydranal solution, f, to determine the mass fraction of water, whereby $w_{H20} = f \cdot v_{KF}/m_s$. However, this does not take into account the instrument drift of the system, d, where d is background volume of titrant delivered per unit time (in µL/min). The drift correction (in mL of titrant delivered) for a titration of that takes time t to complete is $d \cdot t/1000$. Thus, the drift corrected mass fraction is:

$$\boldsymbol{w_{H2O}} = \boldsymbol{R} \cdot \frac{\boldsymbol{f} \cdot (\boldsymbol{v_{KF}} - \boldsymbol{d} \cdot \boldsymbol{t}/\boldsymbol{1000}) \cdot \boldsymbol{C}}{\boldsymbol{m_s}}. \quad (3)$$

where parameter *C*, defined to have a value of unity, is used to account for uncertainty in the calibration solution, and *R*, also defined to have a value of unity, is the replication uncertainty.

4.9.1. Mass Fraction Water in SRM 2890a

Six ampoules of SRM 2890a were selected at random for analysis by volumetric Karl Fischer titration and were run in a random order. Measurements of the six ampoules of SRM 2890a plus one ampoule of SRM 2890 control were run over four days. The water mass fraction of all replicates of SRM 2890a measured by volumetric Karl Fischer titration are listed in

Table 9. The table lists the day ran, the box number from where the sample was pulled, the sample mass of each replicate, and the water mass fraction, w_{H2O}, gives the average water mass fraction for each ampoule and its uncertainty, $u(w_{H2O})$. The uncertainty of the ampoule water mass fraction is described below. The mean water mass fraction of SRM 2890a determined volumetric Karl Fischer titration is 47.10 mg/g with a standard deviation of 0.051 mg/g. The water mass fraction of SRM 2890a determined by volumetric Karl Fischer is in good agreement with the value determined by the coulometric method.

The water mass fraction for each ampoule of SRM 2890a measured by volumetric Karl Fischer titration is displayed in Fig. 10 by run order. The figure shows good agreement between the ampoules measured.

Table 9. Results for 6 SRM 2890a Ampoules by Volumetric Karl Fischer Titration.

				mg/g		
Day	Box	m_{2890a}, g	w_{2890a}, mg/g	$\overline{w}_{2890a}$	$s(w_{2890a})$	$u(w_{2890a})$
1	19	0.08572	46.897			
1	19	0.08700	47.149	47.112	0.199	0.209
1	19	0.08371	47.289			
1	4	0.07862	47.067			
1	4	0.08490	46.964	47.114	0.179	0.190
1	4	0.09454	47.312			
2	6	0.04489	47.134			
2	6	0.05339	47.204	47.087	0.146	0.160
2	6	0.06934	46.924			
3	24	0.04900	47.131			
3	24	0.08597	47.129	47.091	0.068	0.094
3	24	0.10749	47.013			
3	17	0.11629	46.981			
3	17	0.09635	47.409	47.115	0.255	0.263
3	17	0.10597	46.955			
4	1	0.10267	46.855			
4	1	0.10275	47.116	46.981	0.131	0.146
4	1	0.11240	46.973			
			N:	6		
			Mean:	47.083		
			Standard Deviation:	0.051		

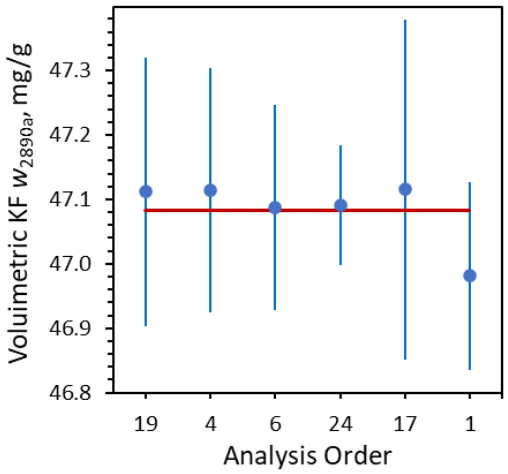


Fig. 10. Volumetric Measurements of 6 SRM 2890a Ampoules.

Each symbol denotes the mean mass fraction water estimate from three replicate measurements of one ampoule of SRM 2890a. Error bars represent the standard uncertainty. The horizontal line represents the grand mean of the measurements.

4.9.2. Mass Fraction Water in SRM 2890

The water mass fraction for the control sample SRM 2890 Water Saturated 1-Octanol was also measured by volumetric Karl Fischer titration. One ampoule was measured and values for water mass fraction of the replicates, and the average mass fraction is given in Table 10, with the uncertainty calculated as above. The average mass fraction of water in SRM 2890 control is 48.07 mg/g with a standard deviation of 0.21 mg/g. An estimate of the expanded uncertainty was calculated as 0.54 mg/g, giving the measured value of the water mass fraction of SRM 2890 control as (48.07 ± 0.54) mg/g. This is in good agreement with the certified value of (47.1 ± 1.0) mg/g water for SRM 2890, where the determined value falls within the expanded uncertainty of the SRM and is in excellent agreement with the value determined by coulometric Karl Fisher [15].

Table 10. Mean Water Mass Fraction for SRM 2890 by Volumetric Karl Fischer titration.

m_{sample}, g	w_{2890}, mg/g	$u(w_{2890})$, mg/g
0.08981	47.84	0.044
0.09645	48.23	0.043
0.10113	48.15	0.043
N:	3	
Mean:	48.07	
Standard Deviation:	0.21	

4.9.3. Uncertainty Components

Uncertainty estimates were evaluated by Type A and Type B methods for each identified uncertainty component of the volumetric Karl Fischer titration; they are listed in Table 11. The

uncertainty of the titer factor, *f*, incorporates the uncertainty of the calibration solution mass fractions and the uncertainty of the calibration solution titrations.

Table 11. Components of Uncertainty in the Volumetric Karl Fischer Measurements.

Measurement	Value	Type [a]	Distribution	range	uncertainty
mass (*m*)	1 g	B	Rectangular	± 0.03 mg [b]	0.017 mg
titration time (*t*)	30 min	B	Normal	± 1 s [c]	0.5 sec
volume of KF reagent titrated (v_{KF})	2 mL	B	Rectangular	± 7 µL [b]	4.041 µL
drift rate (*d*)	1.00 µL/min	B	Rectangular	±0.1 µL/min [c]	0.05 µL/min
Titer factor (*f*)	2.034 µg/mL	A/B	normal	± 0.00973 µg/mL	0.00688 µg/mL
calibrant (*C*)	1	A/B	normal	± 0.00029	0.00058
replication (*R*)	1	A	normal	± 0.00130	0.0011

a A or B identifies whether a Type A or B approach is used to evaluate the standard uncertainty component.
b Values given for the ranges are from the manufacturer. Distributions are assigned by the authors.
c Values given for the ranges are from multiple observations of instrument performance during operations.

An uncertainty for each ampoule is determined using the GUM to propagate errors using Eq. (**3** [11, 12]. These values are given in

Table 9, with the average uncertainty for each ampoule measured using volumetric KF is ~ 0.17 mg/g.

Similarly, the combined standard uncertainty is determined using the GUM to propagate errors using Eq. (**3** [11, 12]. For the volumetric Karl Fischer titrations of SRM 2890a, u_c = 0.19 mg/g. For SRM 2890 control, the combined standard uncertainty is calculated in the same manner and the resultant value is, u_c = 0.13 mg/g.

5. Mass Balance

The water content and 1-octanol organic purity of SRM 2890a were determined using a GC-FID mass balance approach.

5.1. Materials

Six ampoules of SRM 2890a were pulled from boxes 1, 5, 10, 23, 28, and 32. One ampoule of SRM 2890 was used as a control.

Anhydrous 1-octanol was obtained from Sigma-Aldrich. Omnisolve glass distilled grade butyl alcohol (1-butanol) obtained from EM Science was used as the internal standard (IS). HPLC-grade Isopropyl alcohol (2-propanol, IPA) obtained from Supelco was used as a solvent.

A recently calibrated Mettler XPR205 balance was used to prepare calibrants and samples.

5.2. Calibrant Preparation

Eight calibrants (Cal 1 to Cal 8) were independently prepared to quantify 1-octanol in the samples. These calibrants were gravimetrically prepared by diluting 100 µL to 250 µL of 1-octanol and 200 µL of the 1-butanol IS in 40 mL of IPA.

Five solutions, QC-A through QC-E, that were prepared for use in preliminary experiments were used as calibration verification standards. They were prepared by diluting 150 µL to 250 µL of 1-octanol with 200 µL of IS in 40 mL of IPA.

Additional solutions were prepared to demonstrate the GC-FID system's linearity range. Six higher concentration solutions were prepared by adding 3 mL, 2 mL, 2.4 mL, 1 mL, 0.75 mL, and 0.5 mL of 1-octanol to 200 µL of IS to 40 mL of IPA. Nine lower concentration solutions were prepared from a series of stock solutions prepared by 1:10 (volume fraction) serial dilutions, then diluting 200 µL of each stock with 200 µL of IS in 40 mL of IPA.

A blank was prepared by mixing 200 µL of butyl alcohol in 40.2 mL of IPA.

Table 12 lists the 1-octanol mass fractions, w_{oct}, 1-butanol mass fractions, w_{IS}, and the 1-octanol/1-butanol ratios, w_{oct}/w_{IS}, for the calibrants, verification solutions, and extended range solutions.

Table 12. 1-Octanol Quantification, Verification, and Demonstration Solutions.

Quantification and Verification

Solution	w_{oct} g/g	w_{IS} g/g	w_{oct}/w_{IS}
Cal 1	0.006521	0.005151	1.266
Cal 2	0.005860	0.005184	1.130
Cal 3	0.005539	0.005174	1.071
Cal 4	0.005199	0.005187	1.002
Cal 5	0.004962	0.005204	0.953
Cal 6	0.004480	0.005109	0.877
Cal 7	0.003905	0.005183	0.753
Cal 8	0.002625	0.005221	0.503
QC-A	0.006555	0.005170	1.268
QC-B	0.005917	0.005248	1.127
QC-C	0.005307	0.005286	1.004
QC-D	0.004570	0.005170	0.884
QC-E	0.003933	0.005235	0.751

Extended Range Demonstration

Solution	w_{oct} g/g	W_{IS} g/g	w_{oct}/w_{IS}
A1	0.07900	0.005410	14.6
A2	0.06569	0.005372	12.2
E1	0.05217	0.005191	10.1
A3	0.02657	0.005362	4.95
E2	0.01935	0.005212	3.71
A4	0.01386	0.005379	2.58
E3	0.0009495	0.005168	0.184
A5	0.0005305	0.005217	0.102
E4	0.0004016	0.005139	0.0781
E5	0.00010416	0.005093	0.0204
A6	0.00005136	0.005050	0.0102
E6	0.00004266	0.005190	0.00822
E7	0.00001072	0.005163	0.00208
A7	0.000005157	0.005145	0.00100
E8	0.000004335	0.005094	0.000851
blank	0	0.005188	0

5.3. Sample Preparation

Two replicates from six ampoules of SRM 2890a were prepared by diluting 200 µL of material with 200 µL of the 1-butanol IS in 40 mL of IPA. Four replicates from one ampoule of the SRM 2890 control were prepared using the sample procedure. These samples were prepared as shortly as practical after the ampoules were opened.

In addition to the samples prepared for the quantitation of 1-octanol in SRM 2980a, samples were prepared to determine the purity of 1-octanol in 1) the 1-octanol used to prepare calibrants, 2) SRM 2980a, and 3) SRM 2890. This was done by placing approximately 50 µL of sample (1-octanol, SRM 2980a, or SRM 2890) in a 2 mL autosampler vial and then diluting it with IPA to 2 mL. Four purity samples of SRM 2890a and SRM 2890 were prepared from each ampoule. Eight purity samples were prepared from the 1-octanol used to prepare the calibrants.

5.4. Instrumental Methods.

Samples were analyzed by GC-FID using an Agilent 7890A GC. Three separate analyses were performed: 1-octanol measurements on a DB-624 column (Agilent Technologies,Santa Clara, CA), purity assessment on a Rxi-624 column (Restek Corporation, Bellefonte, PA), and purity assessment on a Rxi-1301 column (Restek Corporation). Table 13 lists the method details for each method. An example 1-octanol quantitation chromatogram (Method 1, DB-624 column) is displayed in Fig. 11. Example purity assessment chromatograms (Methods 2 and 3, Rxi-624 and Rxi-1301 columns) are displayed in Fig. 12.

Table 13. Gas Chromatography Method Details.

	Parameter	Method 1 1-Octanol Analysis	Method 2 Purity Assessment	Method 3 Purity Assessment
Column	Manufacturer	Agilent	Restek	Restek
	Phase	DB-624 UI	Rxi-624 sil MS	Rxi-1301 sil MS
	Length, m	30	60	60
	Diameter, mm	0.25	0.25	0.25
	Phase thickness, µm	1.4	1.4	1
Inlet & injection	Injection mode	split	split	split
	Split ratio	50:1	50:1	50:1
	Temperature, °C	250	270	250
	Column flow, mL/min	1	1.5	1
	Septum flow, mL/min	1	1	1
	Injection volume, µL	0.6	0.6	0.6
Oven	Initial temperature, °C	110	40	110
	Initial oven hold time, min	1	1	1
	Oven ramp, °C/min	10	5	5
	Final oven temperature, °C	250	250	225
	Final temperature hold time, min	1	1	5
	Total run time, min	16	44	29
Detector	Temperature, °C	270	270	250
	H_2 flow, mL/min	34	34	34
	Air flow, mL/min	375	375	375
	N_2 makeup flow, mL/min	29	28.5	29
	Column + makeup flow, mL/min	30	30	30
	Data acquisition rate	50	50	50

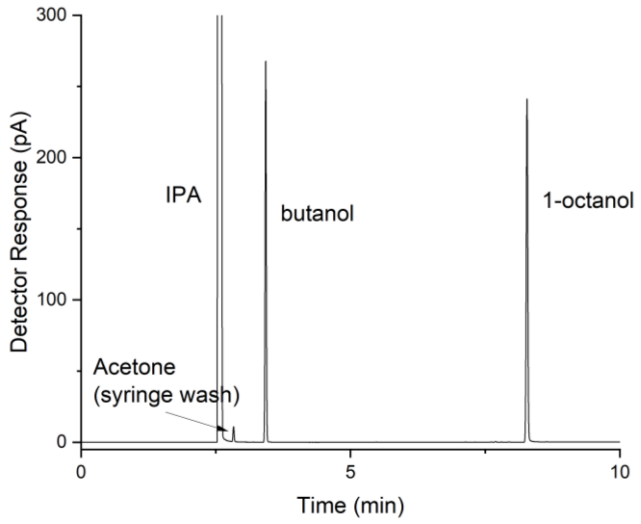


Fig. 11. Example Quantitation Chromatogram for SRM 2890a.

The chromatogram was obtained using the DB-624 column (Method 1). At this graphical resolution, the baseline continues structureless past 10 min.

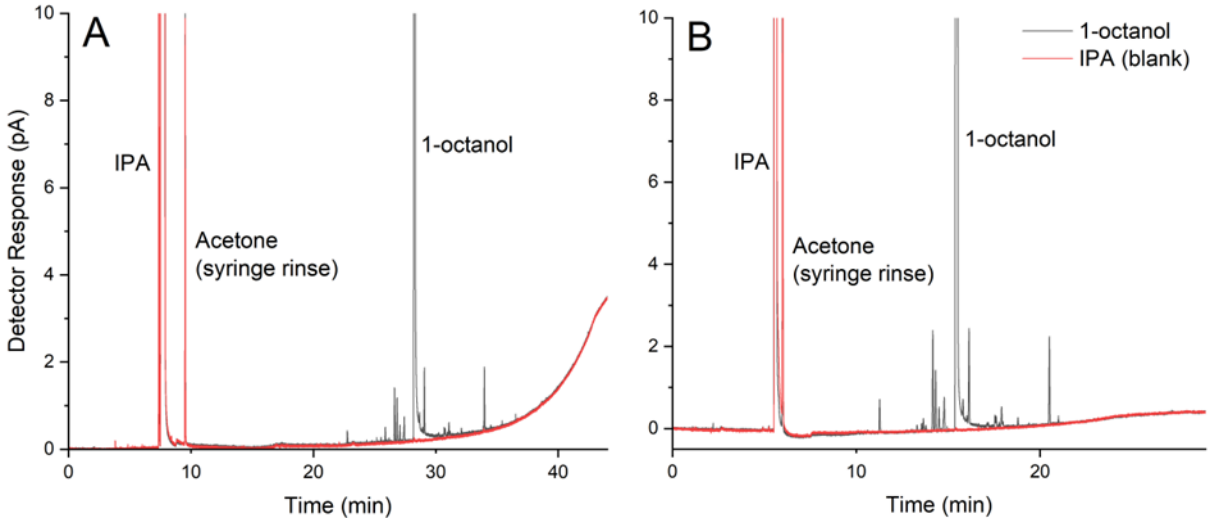


Fig. 12. Example Purity Assessment Chromatograms for the 1-Octanol Standard.

The black curves display gas chromatograms of the 1-octanol used to prepare the calibrants. The overlayed red curves display chromatograms of the solvent (IPA). The chromatograms in Panel A were obtained using the Rxi-624 column (Method 2). The chromatograms in Panel B were obtained using the Rxi-1301 column (Method 3). The Y-axis-scale in both Panels is expanded to show the impurity peaks.

5.5. Quantitation

The GC-FID chromatograms were analyzed using OpenLab CDS ChemStation Edition for GC Systems Rev C.01.04C35 (Agilent Technologies).

The FID peak area response (A_{oct}) is known to be proportional to the mass of ionized carbon in the flame [17]. To confirm linearity, solutions were prepared to span an extended range of hydrocarbon content using the 1-octanol calibration standard as the hydrocarbon source since all likely organic impurities in the 1-octanol materials investigated are related hydrocarbons. As shown in Fig. 13, A_{oct} as determined from the Method 1 chromatograms is proportional to the mass fraction of 1-octanol in the solution (w_{oct}) over the entire range investigated.

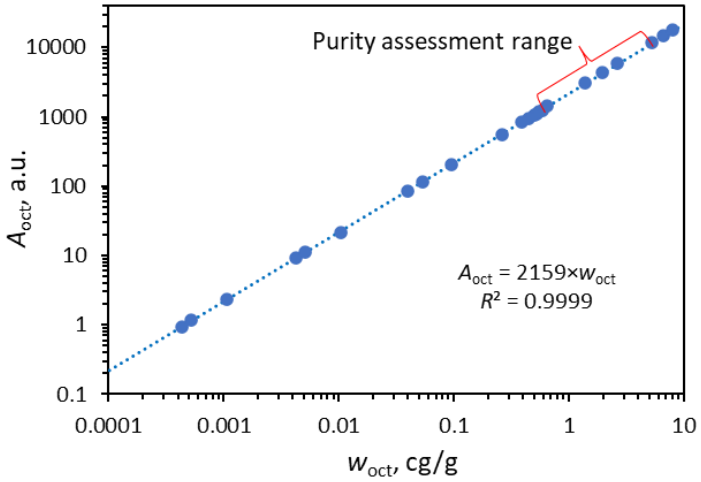


Fig. 13. FID Peak Area as a Function of Mass Fraction 1-Octanol Standard in Calibrant.

5.5.1. Organic Purity Assessment

Organic purity measurements by GC-FID using two different columns were made on SRM 2980, SRM 2890a, and the 1-octanol used to prepare the calibrants. Two blanks were run in between each sample.

To determine the percent of 1-octanol in the organic constituents of these samples, the total area of all peaks in the chromatogram except for peaks also found in the IPA solvent blanks, A_{tot}, and the area of octanol peak, A_{oct}, were determined. There are impurity peaks within the tail of the 1-octanol peaks in the Method 2 and Method 3 chromatograms (see Fig. 12). The area of the impurities in the tail of the 1-octanol peak were determined using a tangent skim. For each chromatogram, the purity of the 1-octanol in the organic portion of a material is estimated as:

$$\boldsymbol{P_{\mathrm{FID}} = \frac{A_{\mathrm{oct}}}{A_{\mathrm{tot}}}}. \qquad (4)$$

The consensus organic purity and its uncertainty were estimated by treating the analysis on the two different columns as two methods and combining them using the DerSimonian-Laird model implemented in the NIST Consensus Builder (NICOB) [18]. The inputs to the model were the mean of the replicate purity measurements on each column and the associated standard deviation of the mean (standard deviation of the replicates divided by the square root of the number of replicates).

Table 14 lists the 1-octanol organic purity measurement values (P_{FID}) for the 1-octanol standard used to prepare the calibrants, SRM 2890, and SRM 2890a, as well as the measurement mean ($\bar{P}_{\mathrm{FID}}$), standard deviation ($s(P_{\mathrm{FID}})$), and standard uncertainty of the mean ($u(\bar{P}_{\mathrm{FID}})$) estimated as $s(P_{\mathrm{FID}})/\sqrt{n}$ where *n* is the number of measurements. Table 14 also lists the DerSimonian-Laird means ($\bar{\bar{P}}_{\mathrm{org}}$) and standard uncertainties ($u(\bar{\bar{P}}_{\mathrm{FID}})$) for the three materials.

Table 14. GC-FID Organic Purity of Calibrant and SRMs 2890 and 2890a, g/(100 g).

	Method 2 (Rxi-624)				Method 3 (Rxi-1301)				Consensus	
Material	P_{FID}	$\bar{P}_{\mathrm{FID}}$	$s(P_{\mathrm{FID}})$	$u(\bar{P}_{\mathrm{FID}})$	P_{FID}	$\bar{P}_{\mathrm{FID}}$	$s(P_{\mathrm{FID}})$	$u(\bar{P}_{\mathrm{FID}})$	$\bar{\bar{P}}_{\mathrm{FID}}$	$u(\bar{\bar{P}}_{\mathrm{FID}})$
Standard 1-Octanol	99.4203 99.4141 99.4210 99.4172	99.4182	0.0032	0.0016	99.3742 99.3650 99.3514 99.3702	99.3652	0.0099	0.0050	99.393	0.027
SRM 2890	99.5394 99.5492	99.5443	0.0069	0.0049	99.5391 99.5275	99.5333	0.0082	0.0058	99.5392	0.0055
SRM 2890a	99.0009 99.0015 99.0075 99.0058 99.0074 99.0037	99.0045	0.0029	0.0012	98.9550 98.9731 98.9710 98.9443 98.9721 98.9672	98.964	0.012	0.0047	98.984	0.020

5.5.2. 1-Octanol Mass Fraction Assessment

The twelve SRM 2890a replicates, four SRM 2890 control replicates, eight bracketing quantitation calibrants, and five calibration verification solutions were analyzed in a pre-determined random order. Second injections were then analyzed in reverse order.

Because GC-FID does not detect water, the above organic purity assessment does not account for the water content of the 1-octanol used to prepare the calibrants. The small mass fraction of water in the calibrant standard ($w_{H2O,Std}$) was previously determined by coulometric KF to be 0.0616 mg/g with a standard uncertainty of 0.0016 mg/g. Assuming that the only significant components of the 1-octanol standard used to prepare the calibration and verification solutions are 1-octanol, its hydrocarbon impurities, and water, the mass fraction of 1-octanol in the standard ($w_{oct,Std}$) is:

$$\begin{aligned} \boldsymbol{w_{\mathbf{oct,Std}}} &= \left(\mathbf{1} - \boldsymbol{w_{\mathbf{H2O,Std}}}\right)\frac{\bar{\bar{\boldsymbol{P}}}_{\mathbf{FID,Std}}}{\mathbf{100}} \\ &= \left(\mathbf{1} - (\mathbf{0.0000616} \pm \mathbf{0.0000016})\right)\frac{(\mathbf{99.393} \pm \mathbf{0.027})}{\mathbf{100}} \\ &= (\mathbf{0.99387} \pm \mathbf{0.00027})\ \mathbf{g/g}. \end{aligned} \tag{5}$$

5.5.2.1. Calibration Model

A linear calibration model was constructed using Cal 1 through Cal 8:

$$\frac{\boldsymbol{A_{\mathbf{oct}}}}{\boldsymbol{A_{\mathbf{IS}}}} = \boldsymbol{\alpha} + \boldsymbol{\beta}\ \frac{\boldsymbol{m_{\mathbf{Std}}}\boldsymbol{w_{\mathbf{oct,Std}}}}{\boldsymbol{m_{\mathbf{IS}}}} \tag{6}$$

where A_{oct} is the 1-octanol peak area in the chromatogram, A_{IS} is the IS peak area, m_{Std} is the mass of the 1-octanol standard in the calibrant, and m_{IS} is the mass of the 1-butanol IS in the calibrant. Since the mass ratios are much less variable than the peak area ratios, the intercept and slope parameters were determined using ordinary least squares regression: α = -0.0109 ± 0.0035 and β = 1.2367 ± 0.0036. The coefficient of determination (R^2) is 0.99995 and the standard uncertainty of prediction (average residual) is 0.0022.

Table 15 lists the peak area and sample preparation data for the eight calibration solutions used to parameterize the model and the five QC solutions used to verify the parametrization. The model and its residuals are displayed in Fig. 14.

The predicted peak area ratios agree well with the measured values. The maximum relative difference for the QC solutions is less than 0.2 %.

Table 15. Calibration Model and Calibration Verification Data.

	Peak Area-Related Information					Mass-Related Information			Calibration Model-Related Information			
ID [a]	A_{oct} a.u.	A_{IS} a.u.	A_{oct}/A_{IS}	$\overline{A_{oct}/A_{IS}}$ [b]	$s(A_{oct}/A_{IS})$ [c]	m_{Std} g	m_{IS} g	$w_{oct,Std} \times m_{std}/m_{IS}$	$\widehat{A_{oct}/A_{IS}}$ [d]	Δ [e]	$\bar{\Delta}$ [f]	$s(\Delta)$ [g]
Cal 1:1	664.76	428.71	1.5506	1.5537	0.0045	0.20792	0.16323	1.2660	1.5548	0.0042	0.0010	0.0045
Cal 1:2	676.35	434.42	1.5569							-0.0021		
Cal 2:1	602.53	433.49	1.3900	1.3882	0.0025	0.18624	0.16374	1.1304	1.3871	-0.0028	-0.0011	0.0025
Cal 2:2	597.66	431.07	1.3864							0.0007		
Cal 3:1	564.94	432.05	1.3076	1.3101	0.0036	0.17574	0.16315	1.0706	1.3131	0.0055	0.0030	0.0036
Cal 3:2	571.53	435.40	1.3126							0.0004		
Cal 4:1	536.55	435.28	1.2327	1.2328	0.0003	0.16529	0.16389	1.0024	1.2287	-0.0039	-0.0041	0.0003
Cal 4:2	536.32	434.95	1.2330							-0.0043		
Cal 5:1	511.70	437.65	1.1692	1.1688	0.0005	0.15753	0.16422	0.9534	1.1682	-0.0010	-0.0006	0.0005
Cal 5:2	499.49	427.49	1.1684							-0.0003		
Cal 6:1	456.05	425.81	1.0710	1.0729	0.0026	0.14400	0.16319	0.8770	1.0737	0.0027	0.0008	0.0026
Cal 6:2	456.23	424.50	1.0747							-0.0010		
Cal 7:1	395.40	430.51	0.9185	0.9200	0.0022	0.12374	0.16322	0.7535	0.9209	0.0025	0.0009	0.0022
Cal 7:2	399.94	433.99	0.9215							-0.0006		
Cal 8:1	265.05	433.16	0.6119	0.6108	0.0016	0.08253	0.16315	0.5027	0.6109	-0.0010	0.0001	0.0015
Cal 8:2	265.16	434.90	0.6097							0.0012		
QC-A:1	671.29	431.47	1.5558	1.5595	0.0052	0.20631	0.16172	1.2679	1.5571	0.0013	-0.0023	0.0052
QC-A:2	675.34	432.04	1.5631							-0.0060		
QC-B:1	609.05	441.38	1.3799	1.3824	0.0035	0.18592	0.16390	1.1274	1.3834	0.0035	0.0010	0.0035
QC-B:2	608.40	439.32	1.3849							-0.0015		
QC-C:1	545.27	442.95	1.2310	1.2293	0.0024	0.16474	0.16310	1.0039	1.2306	-0.0004	0.0013	0.0024
QC-C:2	537.14	437.57	1.2276							0.0030		
QC-D:1	474.91	438.29	1.0836	1.0811	0.0035	0.14442	0.16238	0.8840	1.0823	-0.0013	0.0012	0.0035
QC-D:2	463.61	429.84	1.0786							0.0037		
QC-E:1	407.11	441.81	0.9215	0.9200	0.0021	0.12368	0.16359	0.7514	0.9184	-0.0031	-0.0016	0.0021
QC-E:2	397.24	432.47	0.9186							-0.0002		

a) Solution:Injection

b) Mean of two A_{oct}/A_{IS}

c) Standard deviation of two A_{oct}/A_{IS}

d) Predicted A_{oct}/A_{IS} values for α = -0.0110 and β = 1.2369

e) Difference: $\widehat{A_{oct}/A_{IS}} - A_{oct}/A_{IS}$

f) Mean of two differences

g) Standard deviation of two differences

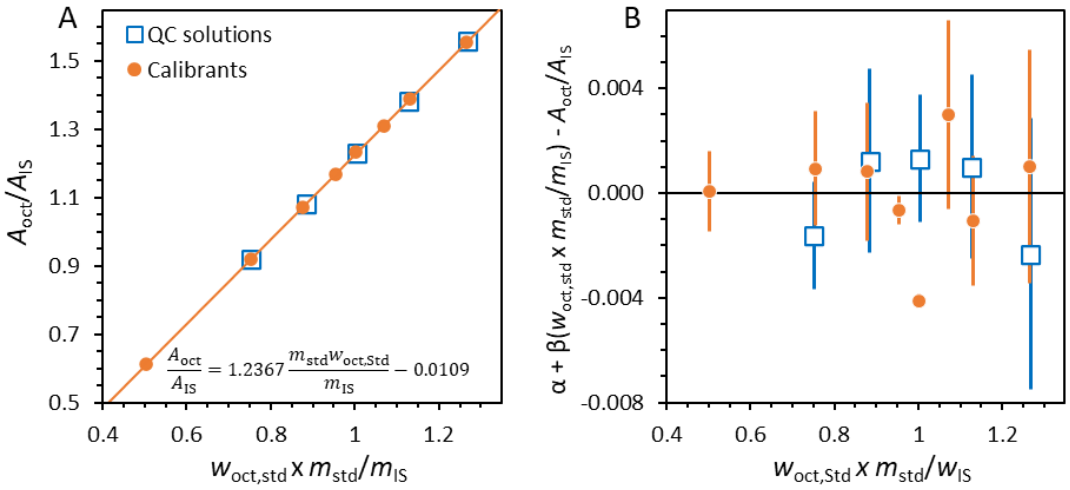


Fig. 14. Calibration Model and Residuals.

The solid circles denote the eight {mass ratio, peak area ratio} calibration values, the open squares denote the five {mass ratio, peak area ratio} values for the QC solutions. Error bars represent standard deviations between two values. Panel A displays the calibration and QC solution values and the calibration model. Panel B displays the residuals between the calculated and observed peak area ratios.

5.5.2.2. Prediction of Mass Fraction 1-Octanol

The mass fraction of 1-octanol in an original SRM 2890 and SRM 2890a sample was determined from the 1-octanol and IS peak areas in the diluted sample, the mass fraction IS in the diluted sample, and the sample dilution factor:

$$\boldsymbol{w_{oct} = w_{IS} \frac{\left(\frac{A_{oct}}{A_{IS}} - \alpha\right)}{\beta} \frac{(m_{sam} + m_{IS} + m_{sol})}{m_{sam}}} \quad (7)$$

where w_{IS} is the mass fraction of the internal standard in the diluted sample, A_{oct} is the area of the 1-octanol peak, A_{IS} is the area of the internal standard peak, m_{sam} is the mass of the original sample in the diluted sample, m_{IS} is the mass of the IS in the diluted sample, and m_{sol} is the mass of the IPA solvent in the diluted sample.

5.5.2.3. Prediction of Mass Fraction Water

Assuming that the only significant components of the SRM materials are 1-octanol, its hydrocarbon impurities, and water, the mass fraction of water is:

$$\boldsymbol{w_{H2O} = 1 - w_{org}} \quad (8)$$

where w_{org} is the mass fraction of total organics (octanol and the hydrocarbon impurities) in the SRM material.

The consensus purity of octanol, $\bar{\bar{P}}_{FID}$, of the two SRMs is described in Section 5.5.1. Given the assumption that the only organic components of the SRMs are 1-octanol and volatile hydrocarbon impurities, the mass fraction of the total organics can be expressed as:

$$w_{org} = \frac{w_{oct}}{\bar{\bar{P}}_{FID}}. \quad (9)$$

The mass fraction of water is then:

$$w_{H2O} = 1 - \frac{w_{oct}}{\bar{\bar{P}}_{FID}}. \quad (10)$$

5.5.3. Mass Fraction 1-Octanol and Water in SRMs 2890 and 2890a

Table 16 lists the peak area and sample preparation data for the twelve SRM 2980a solutions (two aliquots each of six ampoules.

Table 16. Mass Fraction 1-Octanol (w_{oct}) and Water (w_{H2O}) for SRM 2890a Samples.

ID [a]	A_{oct} a.u.	A_{IS} a.u.	A_{oct}/A_{IS}	m_{sam} g	m_{IS} g	m_{sol} g	w_{IS} g/g	DF [b]	w_{oct} g/g	w_{H2O} [c] mg/g
B01-1:1	489.04	433.07	1.1292	0.16231	0.16463	31.31440	0.0052030	194.94	0.93508	55.3
B01-1:2	488.51	430.78	1.1340						0.93899	51.4
B01-2:1	491.88	425.44	1.1562	0.16370	0.16311	31.48315	0.0051276	194.32	0.94027	50.1
B01-2:2	498.37	428.72	1.1625						0.94535	45.0
B05-1:1	490.83	438.66	1.1189	0.16106	0.16549	31.36460	0.0052220	196.77	0.93870	51.7
B05-1:2	487.06	434.05	1.1221						0.94134	49.0
B05-2:1	502.92	434.31	1.1580	0.16479	0.16401	31.19138	0.0052033	191.27	0.94066	49.7
B05-2:2	502.94	433.30	1.1607						0.94288	47.5
B10-1:1	521.07	436.63	1.1934	0.16959	0.16321	31.24315	0.0051688	186.19	0.93714	53.3
B10-1:2	516.16	431.08	1.1974						0.94024	50.1
B10-2:1	510.46	441.34	1.1566	0.16551	0.16507	30.87469	0.0052898	188.54	0.94152	48.8
B10-2:2	501.35	433.37	1.1569						0.94174	48.6
B23-1:1	504.01	432.17	1.1662	0.16460	0.16217	31.17330	0.0051482	191.37	0.93776	52.6
B23-1:2	503.26	430.39	1.1693						0.94022	50.1
B23-2:1	498.73	431.38	1.1561	0.16345	0.16310	31.40370	0.0051402	194.13	0.94164	48.7
B23-2:2	501.61	434.89	1.1534						0.93944	50.9
B28-1:1	499.23	425.43	1.1735	0.16460	0.16175	31.42969	0.0050935	192.93	0.94108	49.3
B28-1:2	493.00	419.64	1.1748						0.94216	48.2
B28-2:1	500.14	431.19	1.1599	0.16380	0.16333	31.17783	0.0051843	192.34	0.94399	46.3
B28-2:2	501.06	431.41	1.1614						0.94521	45.1
B32-1:1	500.56	427.00	1.1723	0.16483	0.16193	31.52350	0.0050841	193.23	0.93987	50.5
B32-1:2	493.28	419.34	1.1763						0.94308	47.2
B32-2:1	509.70	440.18	1.1579	0.16443	0.16379	31.22131	0.0051915	191.87	0.94143	48.9
B32-2:2	499.30	431.73	1.1565						0.94026	50.1
								N:	24	24
								Mean:	0.9408	49.5
								Standard Deviation:	0.0024	2.2

a Box-Aliquot:Injection

b Dilution factor: $(m_{sam} + m_{IS} + m_{sol})/m_{sam}$

c $\bar{\bar{P}}_{FID}$ for SRM 2890a is (98.984 ± 0.020) g/(100 g)

The trend of the w_{H2O} analyses as functions of ampoule Box (an alias for the ampoule production order and of the analysis order are displayed in Fig. 15). The appear to be no significant trend with either Box number or analysis order.

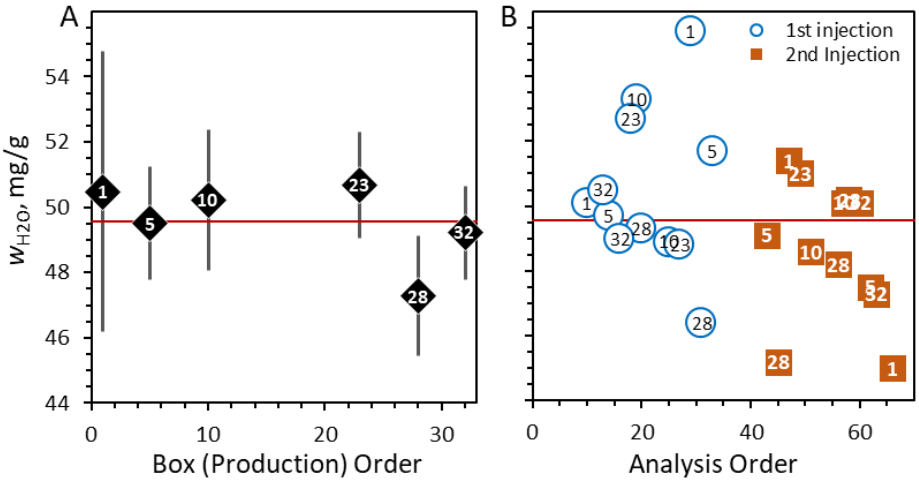


Fig. 15. SRM 2890a Mass Fraction Water (w_{H2O}) as Functions of Box and Analysis Order.

Panel A displays the mean of four w_{H2O} results (two injections each of two aliquots) for the six SRM 2890a ampoules analyzed as a function of the ampoule's box number. Panel B displays the 24 individual results (two injections each of two aliquots for each of the six ampoules) as a function of the order of analysis. The open circles denote the first injection of each aliquot, the solid squares denote the second injection. All symbols are labeled with the ampoule box number. The horizontal lines denote the mean of the mass fraction water, w_{H2O}, measurements expressed in mg/g.

Table 17 lists the peak area and sample preparation data for the four SRM 2980 control solutions (four aliquots from one ampoule).

Table 17. Mass Fraction 1-Octanol (w_{oct}) and Water (w_{H2O}) for SRM 2890 Control Samples.

ID [a]	A_{oct} a.u.	A_{IS} a.u.	A_{oct}/A_{IS}	m_{sam} g	m_{IS} g	m_{sol} g	w_{IS} g/g	DF [b]	w_{oct} g/g	w_{H2O} [c] g/g
2890-1:1	537.91	440.09	1.2223	0.17154	0.16264	30.9652	0.0051963	182.46	0.94539	50.2
2890-1:2	527.62	432.67	1.2195						0.94324	52.4
2890-2:1	518.38	429.13	1.2080	0.16881	0.16209	31.2681	0.0051296	187.19	0.94633	49.3
2890-2:2	520.53	430.30	1.2097						0.94766	48.0
2890-3:1	511.25	430.25	1.1883	0.16769	0.16340	31.3985	0.0051498	189.22	0.94483	50.8
2890-3:2	514.16	430.27	1.1950						0.95010	45.5
2890-4:1	502.03	427.32	1.1748	0.16452	0.16194	31.3013	0.0051202	192.24	0.94373	51.9
2890-4:2	505.99	430.07	1.1765						0.94509	50.5
								N:	8	8
								Mean:	0.9458	49.8
								Standard Deviation:	0.0022	2.2

a SRM-Aliquot:Injection

b Dilution factor: $(m_{sam} + m_{IS} + m_{sol})/m_{sam}$

c $\bar{\bar{P}}_{FID}$ for SRM 2890 is (99.5392 ± 0.0055) g/g

6. Comparison of Mass Fraction Water (w_{H2O}) estimates for SRMs 2890 and 2890a

The coulometric Karl Fischer (KF) estimates of mass fraction water (w_{H2O}) from Section 4.8, volumetric KF from Section 4.9, and mass balance estimates from Section 5.5.3 are displayed in Fig. 16. The mass balance estimates are much more variable than those provided by KF.

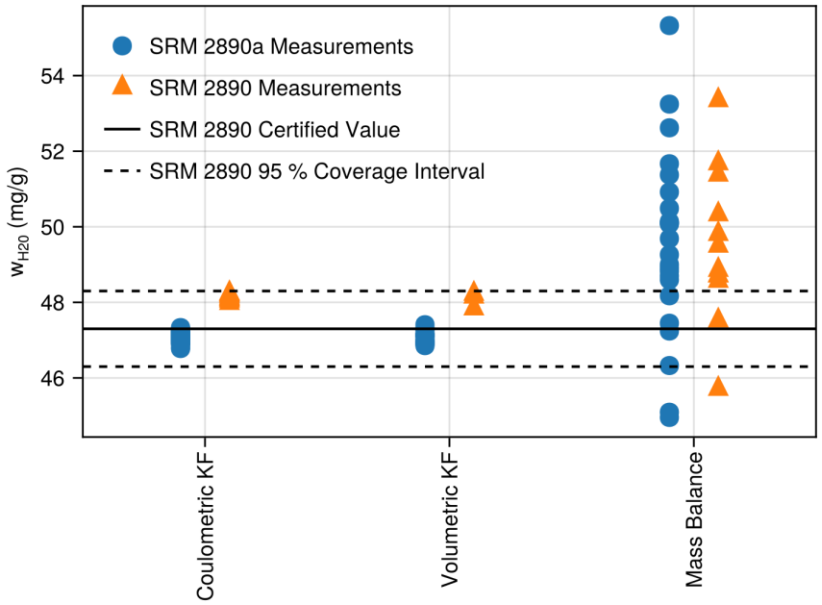


Fig. 16. Comparison of Mass Fraction Water (w_{H2O}) Estimates for SRM 2890 and 2890a.

The figure shows a comparison coulometric Karl Fischer (KF), volumetric KF, and mass balance estimates of mass fraction water (w_{H2O}) in samples SRM 2890a (circles, ●) and SRM 2890 control samples (triangles, ▲). Also shown is certified mass fraction of SRM 2890 (solid line) and the upper and lower limits of the expanded uncertainty. Solid circles denote coulometric Karl Fischer (KF), volumetric KF, and mass balance measurements of the mass fraction water (w_{H2O}) in SRM 2890a. Triangles denote the measurements for SRM 2890.

From Fig. 16 the mass balance estimate of w_{H2O} for SRM 2890a is higher than both the Karl Fischer estimates. Also observed from the figure is that the standard deviations do not overlap, but there is overlap in some of the mass balance data with that of the Karl Fischer measurements of w_{H2O}.

Similarly, Fig. 16 shows that the mass balance estimate of w_{H2O} for SRM 2890 control is higher than both the Karl Fischer estimates. The mass balance estimate of w_{H2O} for SRM 2890 control is also significantly higher than the certified value of w_{H2O} for SRM 2890.

Based on the analysis of the control sample, it is reasonable to state that the observed w_{H2O} from mass balance measurements of SRM 2890 are biased high and the measured w_{H2O} from mass balance for SRM 2890a are likely biased high as well. Results are likely biased high due to biased organic purity determinations by GC-FID, such as not all impurities were accounted for in SRM 2890a and SRM 2890. Also, not all sources of uncertainty may have been accounted for in the mass balance approach. A further analysis of the data for SRM 2890a and the calculation of a consensus mass fraction of water, w_{H2O}, given in section 7.

7. Determination of the Certified Mass Fraction Water (w_{H2O}) for SRM 2890a

The certified mass fraction of water is determined by combining the measurements from all three methods, coulometric Karl Fischer, Karl Fischer volumetric, and GC-FID mass balance into a consensus value. A Bayesian random effects model is used for the combination. Details about the measurements to be combined, the statistical model used to combine them, and the results of the combination are provided in the following subsections, respectively.

7.1. Measurements

In this subsection, the available measurements are reviewed, and some of the notation used in the statistical model is introduced.

The coulometric Karl Fischer measurements were made over a span of six days. On each day, measurements were made on between two and seven ampoules of the candidate material. Three ampoules were measured on multiple days so that day-to-day variability could be estimated separately from ampoule-to-ampoule variability. Over the six days, 24 ampoules were measured, and each time an ampoule was measured, triplicates were taken. A total of 81 measurements were made by coulometry. Let $w_{\mathrm{H20}ijk}^{\mathrm{CKF}}$ represent coulometric measurement $k = 1, 2, 3$, made on ampoule $j = 1, 2, \dots, 24$, on day $i = 1, 2, \dots, 6$.

The volumetric Karl Fischer measurements were made over a span of four days. On each day, measurements were made on one or two ampoules of the candidate material. The same ampoule was never measured on multiple days so that day-to-day variability cannot be estimated separately from ampoule-to-ampoule variability. Over the four days, six ampoules were measured, and each time an ampoule was measured, triplicates were taken. A total of 18 measurements were made by volumetry. Let $w_{\mathrm{H20}\ell m}^{\mathrm{VKF}}$ represent volumetric measurement $m = 1, 2, 3$ made on ampoule $\ell = 1, 2, \dots, 6$.

Measurements by the GC-FID mass balance approach were made on six ampoules of the candidate material. Each ampoule was measured 4 times for a total of 24 measurements. Let $w_{\mathrm{H20}no}^{\mathrm{MB}}$ represent mass balance measurement $o = 1, 2, 3, 4$ made on ampoule $n = 1, 2, \dots, 6$.

7.2. Statistical Model

The measurements are modeled on the logarithmic scale so that assumptions of normality are more tenable because mass fraction is nonnegative. Fitting of the statistical model is done under the Bayesian inference paradigm [19] using Markov Chain Monte Carlo and Stan [20] for the computation. The statistical model is defined in Eq. (11.

$$
\begin{aligned}
\log w_{\mathrm{H20}ijk}^{\mathrm{CKF}} &= \mu + C + D_i + A_j^{\mathrm{CKF}} + \varepsilon_{ijk}^{\mathrm{CKF}} \\
\log w_{\mathrm{H20}\ell m}^{\mathrm{VKF}} &= \mu + V + A_\ell^{\mathrm{VKF}} + \varepsilon_{\ell m}^{\mathrm{VKF}} \\
\log w_{\mathrm{H20}no}^{\mathrm{MB}} &= \mu + B + A_n^{\mathrm{MB}} + \varepsilon_{no}^{\mathrm{MB}} \\
C &\sim \mathrm{Normal}(0, \sigma_{\mathrm{method}}^2) \\
V &\sim \mathrm{Normal}(0, \sigma_{\mathrm{method}}^2) \\
B &\sim \mathrm{Cauchy}(0, \sigma_{\mathrm{method}}^2) \\
D_i &\sim \mathrm{Normal}\left(0, \sigma_{\mathrm{day}}^2\right) \\
A_j^{\mathrm{CKF}} &\sim \mathrm{Normal}\left(0, \sigma_{\mathrm{ampoule}}^2\right) \\
A_\ell^{\mathrm{VKF}} &\sim \mathrm{Normal}\left(0, \sigma_{\mathrm{ampoule}}^2\right) \\
A_n^{\mathrm{MB}} &\sim \mathrm{Normal}\left(0, \sigma_{\mathrm{ampoule}}^2\right) \\
\varepsilon_{ijk}^{\mathrm{CKF}} &\sim \mathrm{Normal}(0, \sigma_{\mathrm{CKF}}^2) \\
\varepsilon_{\ell m}^{\mathrm{VKF}} &\sim \mathrm{Normal}(0, \sigma_{\mathrm{VKF}}^2) \\
\varepsilon_{no}^{\mathrm{MB}} &\sim \mathrm{Normal}(0, \sigma_{\mathrm{MB}}^2)
\end{aligned}
\tag{11}
$$

In Eq. (11, the $\sim$ symbol means *is distributed as*, so $C \sim \mathrm{Normal}(0, \sigma_{\mathrm{method}}^2)$ means that C follows a normal distribution with a mean of 0 and a standard deviation of σ_{method}. All of the parameters and random variables in Eq. (11 relate to the three data sets. The overall mean of the three data sets, on the log-scale, is represented by μ. The random variables C, V, and B, with the corresponding scale parameter σ_{method}, represent the method effect (mean shift due to the measurement method) of the coulometric Karl Fischer, volumetric Karl Fischer, and mass balance measurements, respectively. The D_i random variables, with corresponding standard deviation σ_{day}, account for day-to-day differences in the coulometric Karl Fischer measurements. Even though the volumetric Karl Fischer measurements were made on more than one day, the day-to-day differences are confounded with ampoule-to-ampoule differences for that data set and are not estimated. The A_j^{CKF}, A_ℓ^{VKF}, and A_n^{MB} random variables, with corresponding standard deviation $\sigma_{\mathrm{ampoule}}$, represent ampoule-to-ampoule differences in the coulometric Karl Fischer, volumetric Karl Fischer, and mass balance measurements, respectively. Ampoule-to-ampoule differences may also be interpreted as material heterogeneity, where $\sigma_{\mathrm{ampoule}}$ quantifies, in a single number, the severity of heterogeneity, with zero meaning no heterogeneity, and larger values, increasing severity. The random variables $\varepsilon_{ijk}^{\mathrm{KFC}}$, $\varepsilon_{\ell m}^{\mathrm{KFV}}$, and $\varepsilon_{no}^{\mathrm{MB}}$, with corresponding standard deviations σ_{KFC}, σ_{KFV}, and σ_{MB}, represent other measurement errors for the coulometric KF, volumetric KF, and mass balance measurements, respectively.

The method effect of the mass balance measurements (B) is assigned a Cauchy distribution instead of a Normal distribution, as for C and V, to down-weight the contribution of the mass balance measurements on the overall log-scale mean. This is done because the mass balance

measurements are expected to be higher on average than the coulometric Karl Fischer and volumetric Karl Fischer measurements because there is evidence that not all of the organic impurities were accounted for. This would result in a smaller observed mass fraction of the organics and a larger observed mass fraction of water.

7.2.1. Priors

Since model fitting is done from the Bayesian perspective, prior distributions must be assigned to the parameters of Equation (11. For σ_{method}, σ_{day}, σ_{ampoule}, σ_{CKF}, and σ_{VKF} the half-Normal $(0,0.01^2)$ distribution with support on $\mathbb{R}_+$ is used. For σ_{MB} the half-Normal $(0, 0.05^2)$ distribution with support on $\mathbb{R}_+$ is used. The interpretation of those prior distributions is that the relative standard deviation of the variability in the data accounted for by the corresponding source should be less than 2 % (or 10 % for σ_{MB}) with probability 95 %. Modeling the log scale of the measurements permits the interpretation of the standard deviation parameters as relative standard deviations. All other parameters are assigned flat improper priors to express a lack-of-knowledge a priori.

7.2.2. Goodness-of-fit

The assessment of goodness-of-fit for Eq. (11 is done by comparing the measurements to their posterior predictive distributions (Gelman et al., 2013). FigureFig. 17 shows the coulometric Karl Fischer, volumetric Karl Fischer, and mass balance measurements as small grey points, as well as 95 % prediction intervals for a new hypothetical coulometric Karl Fischer, volumetric Karl Fischer, or mass balance measurement from a new randomly sampled ampoule of candidate SRM 2890a material, made on a new randomly selected day for coulometry as solid vertical lines. Panel B of Fig. 17 is a zoomed in version of panel A for only the coulometric Karl Fischer and volumetric Karl Fischer measurements. The model fits well if approximately 95 % of the observed measurements are enveloped by the prediction intervals (solid vertical lines). All 18 volumetric Karl Fischer measurements are enveloped by the corresponding prediction interval, but 3 out of the 81 coulometric Karl Fischer measurements, and 1 of the 24 mass balance measurements fall outside of the corresponding 95 % prediction intervals. Overall, 97 % of the measurements fall within the 95 % prediction intervals. Thus, the model seems to be an appropriate description of the observed measurements. Figure Fig. 17 also shows an estimate of e^{μ}, which is the proposed certificate value, by the solid horizontal line and a 95 % coverage interval for e^{μ} by the dashed horizontal lines.

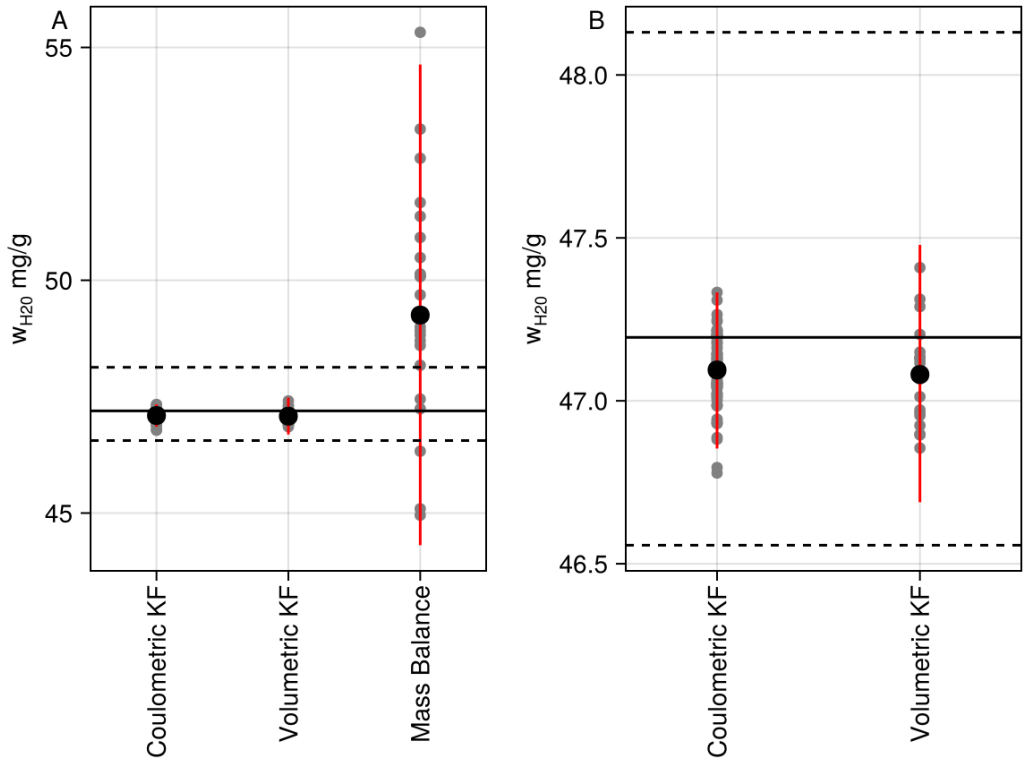


Fig. 17. SRM 2890a Mass Fraction Water (w_{H2O}) as Functions of Measurement Method.

Panel A displays the measurements for each method (small grey points), measurement method median values (large black points), prediction intervals for a new hypothetical measurement from each method (solid vertical lines), the overall median value (solid horizontal line), and a 95 % coverage interval for the overall median value (dashed horizontal lines). Pale B is exactly the same as panel A but zoomed into only the coulometric KF and volumetric KF measurement methods.

7.3. Certificate Value

The measurement equation is

$$e^{\mu} \tag{12}$$

with μ defined in Eq. (11. Equation (12 simply translates log-scale units back to mg/g. The posterior distribution of Eq. (12 quantifies uncertainty in the proposed certificate value. No additional sources of uncertainty assessed by Type B methods are considered. The proposed value is 47.19 mg/g with and expanded uncertainty ($k = 2$) of 0.74 mg/g. Note that the certificate is the only source for the certified value.

The proposed uncertainty for SRM 2890a is smaller than the expanded uncertainty of ± 1.0 mg/g that was given for SRM 2890 [2], and it is fit-for-purpose when using the material as a water standard as intended.

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Appendix A. List of Symbols and Acronyms

A.1. Symbols

d drift rate

m_{sample} mass of sample

t titration time

$u(\cdot)$ standard uncertainty in a quantity

$\overline{w}(\cdot)$ daily average of mass fraction water in a material

w_{2890} mass fraction water in the SRM 2890 control

w_{2890a} mass fraction water in SRM 2890a

w_{CO2} mass fraction carbon dioxide in water

w_{IS} mass fraction 1-butanol internal standard in octanol calibrant

w_{H2O} mass fraction water in generic sample

w_{oct} mass fraction 1-octanol in octanol calibrant

w_{WSO2} mass fraction water in WSO2 daily control material

w_i mass fraction water in the i^{th} ampoule

A.2. Acronyms

IC Ion Chromatography

IPA Isopropyl Alcohol (Propan-2-ol)

KF Karl Fischer water determination techniques

NIST National Institute of Standards and Technology

ORM NIST's Office of Reference Materials

PTFE Teflon® polytetrafluoroethylene

SRM Standard Reference Material, a certified reference material provided by NIST

WSO water saturated 1-octanol

WSO2 a secondary WSO control material