TÜBİTAK
ULUSAL METROLOJİ ENSTİTÜSÜ

Certification Report

Sulfur in Diesel
UME CRM 1203-1
UME CRM 1203-2

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Date
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ABBREVIATIONS AND SYMBOLS

ANOVA	Analysis of Variance
α	Significance Level
ERM	European Reference Material
HR	High Resolution
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ID	Isotope Dilution
ISO	International Standards Organization
k	Coverage Factor
STS	Short-Term Stability
$MS_{between}$	Between-Units Mean Square (ANOVA)
MS_{within}	Within-Unit Mean Square (ANOVA)
NIST	National Institute of Standards and Technology
n	Number of replicates
RSD	Relative Standard Deviation
s	Standard Deviation
s_{bb}	Between-Units Standard Deviation (ANOVA)
$s_{bb,rel}$	Between-Units Relative Standard Deviation
SGT	Single Grubbs Test
SI	Standards Internationale
CRM	Certified Referans Material
s_w	Within-Unit Standard Deviation (ANOVA)
s_{wb}	Within-Bottle Standard Deviation
$s_{wb,rel}$	Within-Bottle Relative Standard Deviation
$\bar{t}$	Mean of the Time Points
t_α	Two-Tail Critical *t* value (t test)
t_i	Time Point for Each Replicate
u_{bb}	Standard Uncertainty Related to Possible Between-Bottle Heterogeneity
$u_{bb.rel}$	Relative Standard Uncertainty Related to Possible Between-Bottle Heterogeneity
u^*_{bb}	Standard Uncertainty of Heterogeneity that Can Be Hidden by Method Repeatability
$u^*_{bb,rel}$	Relative Standard Uncertainty of Heterogeneity that Can Be Hidden by Method Repeatability
u_{char}	Standard Uncertainty Related to Characterisation
$u_{char,rel}$	Relative Standard Uncertainty Related to Characterisation

LTS	Long-Term Stability
u_{lts}	Standard Uncertainty Related to Long Term Stability
$u_{lts,rel}$	Relative Standard Uncertainty Related to Long Term Stability
u_{sts}	Standard Uncertainty Related to Short Term Stability
$u_{sts,rel}$	Relative Standard Uncertainty Related to Short Term Stability
UV	Ultraviolet
$v_{MSwithin}$	MS_{within} degree of freedom
WD-XRF	Wavelength Dispersive X-Ray Fluorescence Spectrometry

ABSTRACT

In this project, production of certified reference materials (CRMs) used in the quality control of sulfur measurements in diesels and the method validation studies has been carried out. As known, source of SO_2 in air causing acid rains is mainly the sulfur emissions by fossil fuels. Environmental concerns about the sulfur emissions resulting from the use of fossil fuels led to regulation of sulfur levels. European Comission regulation published in 1993 puts limit to the level of sulfur in gasoline and diesel fules at 500 mg/kg and 2000 mg/kg, respectively. In 2009, the limit values for both fuel types were updated as 10 mg/kg. Such limitations in the level of sulfur in fuels raised the importance of reliability of measurements and quality controls. The production of CRMs in this project aimed to provide the materials in order to improve the reliability of sulfur measurements in diesel fuel.

INTRODUCTION

Sulfur in diesel CRMs considering Directive 2003/17/EC of the European Parliament and of the Council [1] were produced. Production was performed using TÜBİTAK UME infrastructure in accordance with the ISO Guide 34 [2] ve ISO Guide 35 [3] guidelines. The following studies were undertaken:

- Decision of the methods to be used in the study, and validation of the methods
- Processing the material, and performing homogeneity, stability, commutability and characterization tests.
- Preparation of the certificate and certification report.

Series of certified reference materials for sulfur in various fuels (NIST SRM 1624d, SRM 2723b, SRM 2770, SRM 2771, ERM EF211, EF212, EF213, EF673a and EF674a) are available in the market. Using these materials, reliable measurements of sulfur levels in fuels are performed. Considering the domestic consumption capacity and the difficulties in importing these CRMs from international market, producing the materials using available resources is important. Production of CRMs in Turkey to meet the demand helps to overcome supply problems and makes TUBITAK UME utilize its experience in related fields.

PARTICIPANTS

Participant laboratories involved in the production of CRM and their contributions are listed in Table 1.

Table 1. Participant Laboratories

Work Package	Participants
Sampling and processing	• TÜBİTAK UME • TÜPRAŞ İzmit Refinery Laboratory
Homogeneity study	• TÜBİTAK UME • OMV POAŞ Haramidere Terminal Laboratory
Stability study	• TÜBİTAK UME • OMV POAŞ Haramidere Terminal Laboratory
Project management and data evaluation	• TÜBİTAK UME
Characterization study	• TÜBİTAK UME
Commutability study	• TÜBİTAK UME • OMV POAŞ Antalya Terminal Laboratory • OMV POAŞ Haramidere Terminal Laboratory • OMV POAŞ Trabzon Terminal Laboratory • OPET Petrolcülük A.Ş. Fuel Laboratory Marmara Laboratory

Work Package	Participants
	• TÜPRAŞ İzmit Refinery Laboratory
Density measurements	• TÜBİTAK UME

MATERIAL PROCESSING

Candidate reference material were obtained from TÜPRAŞ İzmit Refinery. Two different diesel samples with approximate sulfur levels of ~30 mg/kg (72 L) and ~3 mg/kg (180 L) were acquired in 18 L volume metal containers. Sulfur level in each container were determined using ICP-MS technique, and the results are given in Table 2.

Table 2. Sulfur levels in raw materials

Containers	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sulfur Mass Fraction (mg/kg)	2.3	2.5	31.7	32.7	32.6	3.2	2.8	3.8	3.1	2.6	32.0	3.0	3.8	2.7

The fuel characterized for sulfur level were filtered through 11 µm porosity filter (Whatman 1001) using vacuum suction to get rid of any partıcular matter. After filtration, the materials were mixed in appropriate volumes in 100 L volume polyethylene tanks to get mixtures in approximate mass fractions of 8 mg/kg and 14 mg/kg for UME CRM 1203-1 and UME CRM 1203-2, respectively. The mixtures were, then, mixed for at least 4 hours to get homogeneous blends.

Bottles with a volume of 125 mL to be used for filling the candidate materials were washed with 15 MΩ·cm Type II water (ELGA Purelab Pulse) and dried in laminar flow cabin prior to filling. The cleaned bottles were checked for any sulfur contamination using ICP-MS. The sulfur levels in blends and in filled bottles were checked and compared, and no significant differences were observed. The results were also compared using the student's t-test concluding that botles does not suffer form any sulfur contamination.

After these controls, the diesel mixtures were filled in the bottles to get at least 100 mL samples in each unit for a total of 700 units for both UME CRM 1203-1 and UME CRM 1203-2. The units were labeled with respect to the filling order, and stored in 4 °C storage room.

HOMOGENEITY

In order to check the homogeneity of the analyte, nine units were selected for both UME CRM 1203-1 and UME CRM 1203-2 using random stratified sampling strategy to represent all units. The number of units selected was decided considering the total number of units in the batch that cubic root of the total count were determined for both candidate materials. The whole batch were divided into equal fragments, and a representative unit was randomly selected from each one. Three replicate sulfur measurements were performed in each selected unit. All the homogeneity tests were performed by OMV POAŞ Haramidere Terminal Laboratory in accordance with TS EN ISO 20884 [4] standard using WD-XRF technique.

Evaluation of the data was performed using one-way Analysis of Variance (ANOVA). The data were statistically checked to see any existence of a trend and/or outlier value. No significant trend were detected for filling order and analytical sequence.

Within unit (s_{wb}) and between units (s_{bb}) homogeneity standard deviation values were calculated using the following equations:

$$s_{wb} = \sqrt{MS_{within}} \quad (1)$$

$$s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}} \quad (2)$$

If $MS_{between}$ is smaller than MS_{within}, s_{bb} cannot be calculated. In this case, u^*_{bb} (standard uncertainty of heterogeneity that can be hidden by method repeatability), is calculated using the following equation:

$$u^*_{bb} = \frac{s_{wb}}{\sqrt{n}} \sqrt[4]{\frac{2}{\nu_{MSwithin}}} \quad (3)$$

Uncertainty data resulting from homogeneity measurements are given in Table 3. The data used in the homogeneity evaluations are given in Appendix 1 as figures.

Table 3. Results of the Homogeneity Study

CRM	$s_{wb,rel}$ (%)	$s_{bb,rel}$ (%)	$u^*_{bb,rel}$ (%)	$u_{bb,rel}$ (%)
UME CRM 1203-1	2.64	1.91	0.88	1.91
UME CRM 1203-2	2.59	0.50	0.86	0.86

STABILITY

Stability studies were performed by simulating creating similar conditions in laboratory to 1) the transfer conditions during the transportation of the material to the customers (short term stability, STS) and 2) storage conditions (long term stability, LTS). Stability tests were performed by OMV POAŞ Haramidere Terminal Laboratory in accordance with the TS EN ISO 20884 standard method using WD-XRF technique.

Similar to the homogeneity study, units for the STS and LTS tests were selected using random stratified sampling technique.

To test the short term stability of the materials, the units were decided to be subjected to temperatures of 18 °C, 35 °C and 50 °C for periods of 1, 2 and 4 weeks. In each of the time period for all 3 temperatures, 2 units for each of the UME CRM 1203-1 and UME CRM 1203-2 were placed in test cabinets. For the reference point, 2 units were selected and kept at reference temperature of 4 °C. At the end of each test period, 2 units from each test cabinet were transfered to reference temperature. When the 4 week-long test period were finished, all the units transferred to the reference temperature were analyzed at the same time.

For the long term stability tests, test units were kept at the reference temperature (4 °C) for periods of 0, 1, 2 and 3 months.

Results of the Short Term Stability Tests:

Evaluations were separately performed for temperatures of 18 °C, 35 °C and 50 °C.

The data at each point were checked for outlier values at 95% and 99% confidence levels using Grubbs test. For each test temperature, measurement data were plotted against the time points, and the data were checked for any significant change over the test period using regression analysis. The calculated slopes of the regression line were tested using two-tailed *t*-test using $t_{\alpha,df}$ as the critical *t* value at α = 0,05 (95% confidence level). The plots are given in Appendix 2.

To test the coherence between the data when plotted against the time, trend lines were plotted. At the end of the *t*-test, no line of which the slope is significantly from zero were observed. The results of the STS measurements performed at 18 °C, 35 °C and 50 °C are given in Table 4.

Table 4. Results of the Short Term Stability Measurements

Parameter		UME CRM 1203-1	UME CRM 1203-2
Is the slope of the regression line significantly different than 0 at 95% and 99% confidence levels?	**18 °C**	No	No
	35 °C	No	No
	50 °C	No	No
Outlier Value*		-	-

*SGT: Single Grubbs Test

As a result of the STS tests, it was concluded that both materials are stable at 18 °C, 35 °C ve 50 °C for a period of 4 weeks. Thus, unless the transfer temperature does not exceed 50 °C and the time does not exceed 4 weeks, the materials can be shipped to the customers without any cooling precautions. The uncertainty values obtained in STS studies are given in Table 5. The uncertainty values obtained from the STS study were insignificant compared to the values obtained from LTS measurements.

Table 5. UME CRM 1203 Short Term Stability Uncertainty Values

Short-Term Stability Uncertainty Values	**UME CRM 1203-1**			**UME CRM 1203-2**		
	18 °C	**35 °C**	**50 °C**	**18 °C**	**35 °C**	**50 °C**
$u_{sts,rel}$ **(%)**	0.38	0.33	0.13	0.69	0.47	0.72

Results of the Long Term Stability Tests:

Storage life of the materials are determined according to the long term stability tests. These tests were performed by keeping 2 units at 4 °C for 0, 1, 2 and 3 month periods and measuring the sulfur levels at the end. Thus, total of 8 units (16 including spare parts) were used for these tests.

The mean of the values obtained at each time point were given Appendix 3. Error bars for each point shows the standard deviation of the values at given point.

The values were plotted against the time and the trend were calculated. The uncertainty value, u_{lts}, obtained from the LTS study and to be used in the value assignmets of the materials, were calculated using the following equation:

$$u_{lts} = \frac{RSD}{\sqrt{\sum(t_i - \bar{t})^2}} \times t \qquad (4)$$

where

RSD : relative standard deviation of the all values obtained in the stability study

t_i : time point for each replicate

$\bar{t}$: mean of the all time points

t : suggested shelf life at 4 °C

The uncertainty values calculated from the STS to be involved in calculation of the assigned value uncertainty at 4 °C and for 12 months are given in Table 6. Plots for the study are given in Appendix 3.

Table 6. LTS results for 12 month shelf life

CRM	**UME CRM 1203-1**	**UME CRM 1203-2**
Is the slope of the regression line significantly different than 0 at 4 °C?	No	No
$u_{lts,rel}$ **(%) for 12 month shelf life at 4 °C**	3.95	3.92

* Values were evaluated at 95% confidence level.

With the results obtained in the study, 4 °C was determined as the storage temperature. To ensure the stability of the material for additional shelf life periods, the materials will be monitored in the post certification period and the results will be reevaluated.

CHARACTERIZATION

According to the ISO Guide 34, characterization study and value assignment can be carried out in different ways. Here, the characterization measurements were performed using a primary measurement method ID-ICP-MS.

The uncertainty of the characterization study, u_{char}, was calculated using the data obtained from the ID-ICP-MS measurements and using the GUM Workbench software.

In the ID-ICP-MS method, the certified reference materials NIST SRM 3154 was used as the calibration standard and IRMM 646 was used as the isotopically enriched spike standard. For the blend preparation the 0,2 g of the diesel sample was mixed with the isotopically enriched standard. The blends were, then, decomposed by clossed vessel microwave digestion (Milestone Ethos Plus) using the setup shown in Figure 1. After the decomposition step, the samples were diluted with deionized water and the $^{32}S/^{34}S$ isotope ratios were measured using HR-ICP-MS (Thermo Element 2) in medium resolution mode.

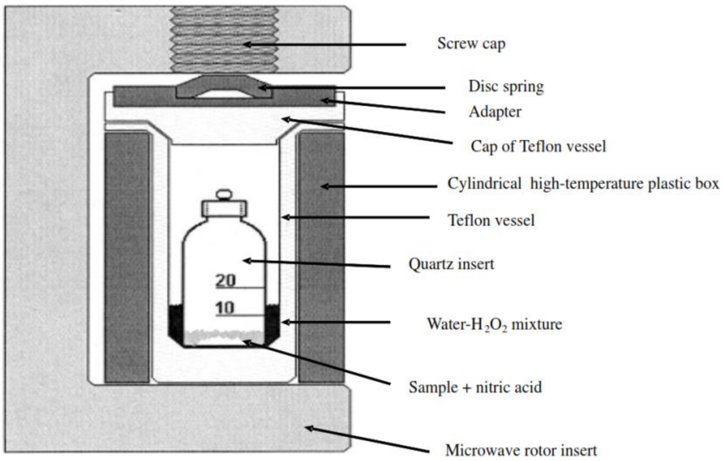

Figure 1. Microwave vessels as used for the decomposition of diesel samples

For the method validation of sulfur measurements NIST SRM 2723b and ERM-EF674a matrix CRMs were used. Recovery values obtained are given in Table 7.

Table 7. Recovery values obtained in metod validation study

Matrix CRM	Certified Value and Uncertainty (mg/kg)	Rep. 1 (mg/kg)	Rep. 2 (mg/kg)	Rep. 3 (mg/kg)	Rep. 4 (mg/kg)	Rep. 5 (mg/kg)	Rep. 6 (mg/kg)	Rep. 7 (mg/kg)	Mean (mg/kg)	Recovery (%)	*RSD* (%)
ERM-EF674a	11.0 ± 0.9	10.86	11.13	10.75	10.67	10.71	10.75	10.87	10.82	98.4	1.4
NIST 2723b	9.06 ± 0.25	8.92	8.81	8.75	8.59	8.87	8.79	8.87	8.8	97.1	1.2

PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT

The uncertainty of the certified value is composed of the uncertainty of the characterization study (u_{char}), uncertainty of the homogeneity (u_{bb}) and the homogeneity of the long term stability (u_{lts}).

These individual uncertainty components are combined using the following equation:

$$U_{CRM} = k \cdot \sqrt{u_{char}^2 + u_{bb}^2 + u_{lts}^2} \tag{5}$$

The uncertainty of the certified value was expanded by a coverage factor of k=*2* for a confidence level 95%. Certified values and associated uncertainties are given in Table 8.

Sertifika değeri üzerindeki genişletilmiş belirsizlik değeri yaklaşık olarak % 95 güvenilirlik aralığını temsil eden kapsam faktörü, =*2* temel alınarak hesaplanmıştır. Sertifika değerleri ve belirsizlikleri Tablo 8'de, her bir parametrenin sertifika değeri üzerindeki belirsizliğe yapmış olduğu yüzde katkısı ise Tablo 9'da verilmiştir.

Table 8. Certified values and uncertainties

CRM	Sulfur Mass Fraction (mg/kg)	U_{CRM} (mg/kg) k = 2	$u_{char,rel}$ (%)	$u_{bb,rel}$ (%)	$u_{lts,rel}$ (%)	$U_{CRM,rel}$ (%) k = 2
UME CRM 1203-1	8.7	0.8	1.1	1.91	3.95	9.05
UME CRM 1203-2	14.5	1.2	0.97	0.86	3.92	8.26

The percent relative contributions from each uncertainty components are given in Table 9.

Table 9. Percent contribution of each parameter to the U_{CRM}

CRM	$u_{bb,rel}$ (%)	$u_{lts,rel}$ (%)	$u_{char,rel}$ (%)
UME CRM 1203-1	27.4	56.8	15.8
UME CRM 1203-2	15.0	68.2	16.9

COMMUTABILITY

The purpose of the commutability study is to prove that the certified parameters of the CRMs are independent of the methods used in the characterization study. In order to conduct the commutability study of the CRMs, ID-ICP-MS results were compared with UV-Fluorescence and WD-XRF methods within the proficiency testing scheme organized by TUBITAK UME in May 2015. Data shown in Table 10 are the values reported by the participant laboratories proving that the comparable results were obtained using different analytical methods.

Table 10. Results of the commutability study

Lab.	UME CRM 1203-1 Sulfur (mg/kg)	UME CRM 1203-2 Sulfur (mg/kg)	Method Used
1	8.7	14.5	ID-ICP-MS
2	7.9	14.0	EN ISO 20846 (UV-Fluorescence)
3	8.0	13.9	EN ISO 20846 (WD-XRF)
4	7.9	13.4	EN ISO 20846 (WD-XRF)
5	9.1	14.6	EN ISO 20846 (UV-Fluorescence)
6	8.1	13.8	EN ISO 20846 (WD-XRF)

DENSITY

Densities of the two materials were measured at (20 ± 1) °C in TÜBİTAK UME according to ISO 12185 standard [5]. Density values given in Table 11 are reported in certificates of the materials as information values.

Table 11. Results of density measurements

CRM	Density (kg/m^3)	Uncertainty (kg/m^3) (k=2)
UME CRM 1203-1	821.65	0.05
UME CRM 1203-2	822.81	0.05

TRACEABILITY

Metrological treceability of the assigned values of the CRMs were provided using NIST SRM 3154 standard. All solution preparations in characterization study were performed gravimetrically using analytical balances controlled before every use with weight sets traceable to TÜBİTAK UME. NIST SRM 2723b and ERM-EF674a matrix certified reference materials were used in method validation studies. Uncertainty estimations of the ID-ICP-MS measurements were calculated using GUM Workbench software.

INSTRUCTIONS FOR USE

Storage conditions

The materials should be stored in between temperatures +2 °C – +8 °C. The bottles should be thoroughly mixed before use in order to exclude the possible effects due to condensation of the material in upper part of the container.

Minimum sample intake

Sample aliquotes of 0.25 mL were used during the characterization measurements, and no between bottle and within bottle inhomogeneity were observed.

Safety Information

Usual laboratory precautions apply. It is strongly recommended that the material must be handled and disposed according to the safety guidelines where applicable. All safety precautions, e.g. working in a fume hood and or using suitable masks, must be taken. All precautions for flammable materials are also valid for this material. Please refer to the Material Safety Datasheet before any use of the material.

REFERENCES

[1] Directive 2003/17/EC of the European Parliament and of the European Council.

[2] International Organization for Standardization, ISO Guide 34, General requirements for the competence of reference material producers, ISO, Geneva (2009).

[3] International Organization for Standardization, ISO Guide 35, Reference materials – General and statistical principles for certification, ISO, Geneva (2006).

[4] TS EN ISO 20884 Petroleum products – Determination of sulphur content of automotive fuels – Wavelength-dispersive X-ray fluorescence spectrometry.

[5] TS EN ISO 12185 Crude petroleum and petroleum products – Determination of density – Oscillating U-tube method, (1996).

REVISION HISTORY

Date	Remark
24.08.2015	First publication.

Appendix 1. Plots for Homogeneity Study

Plots for the homogeneity study of UME CRM 1203-1 and UME CRM 1203-2 are given in Figure 2 and Figure 3, respectively.

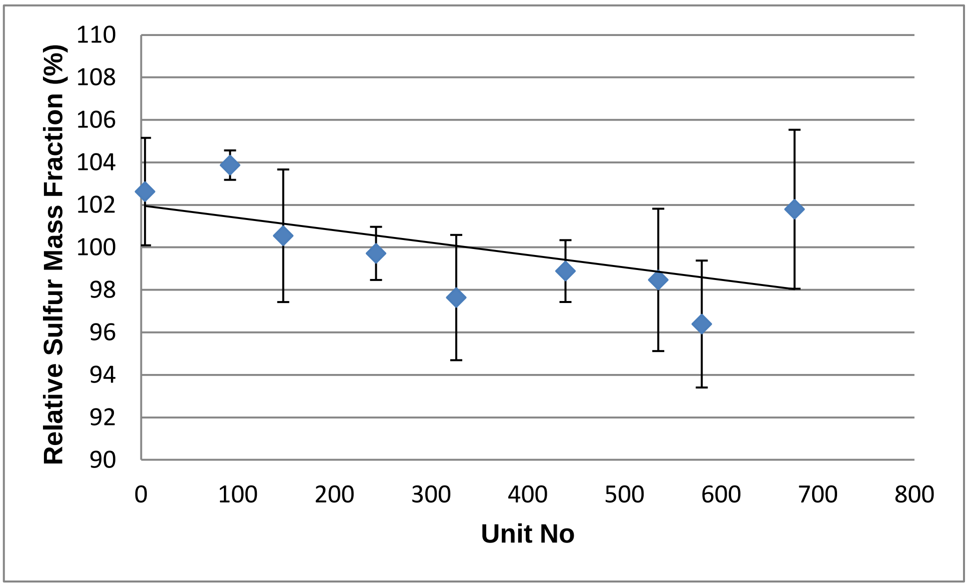

Figure 2. UME CRM 1203-1 homogeneity graph

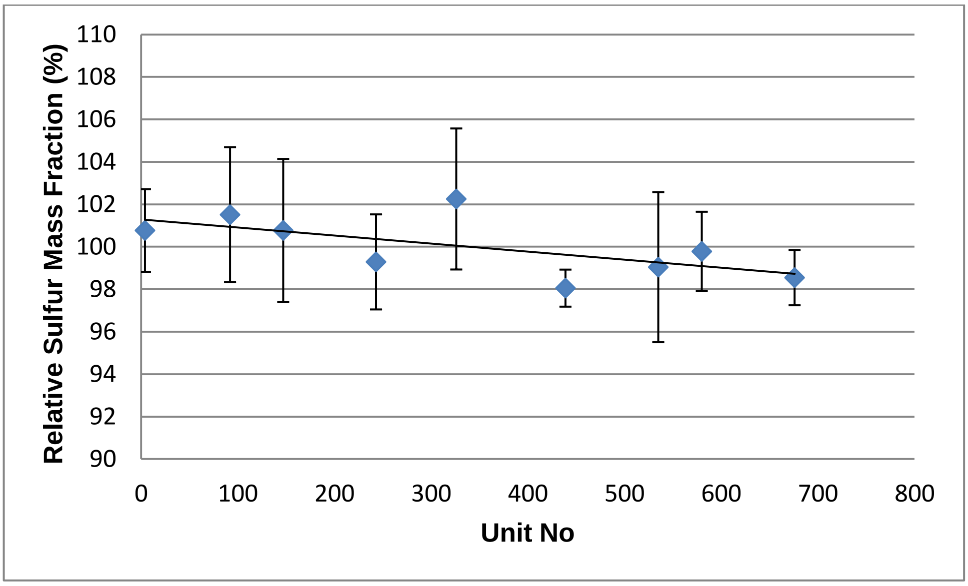

Figure 3. UME CRM 1203-2 homogeneity graph

Note: Error bars in Figures 2 and 3 show the standard deviation of 3 replicate measurements.

Appendix 2. Plots for Short Term Stability Study

Plots for the STS study of UME CRM 1203-1 and UME CRM 1203-2 at 18 °C, 35 °C and 50 °C are given in Figure 4 to Figure 9.

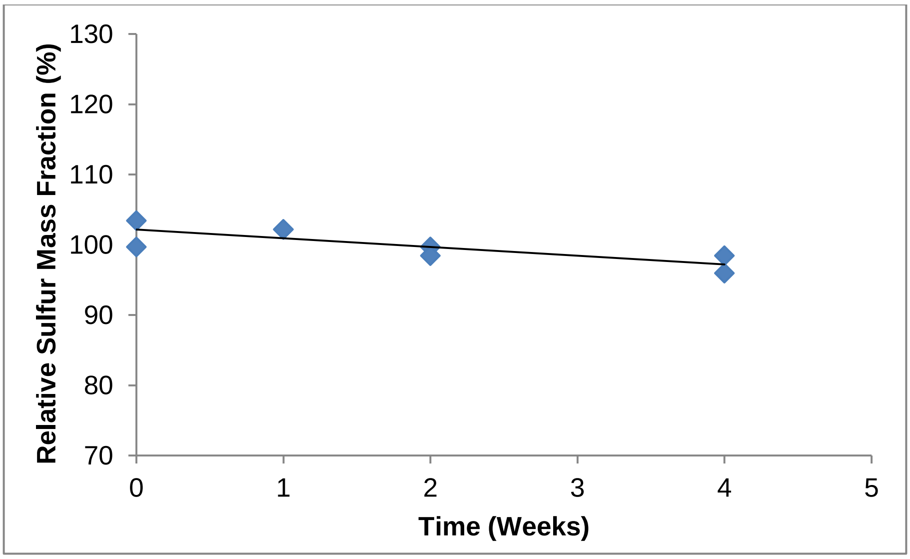

Figure 4. Graph for short term stability of UME CRM 1203-1 at 18 °C

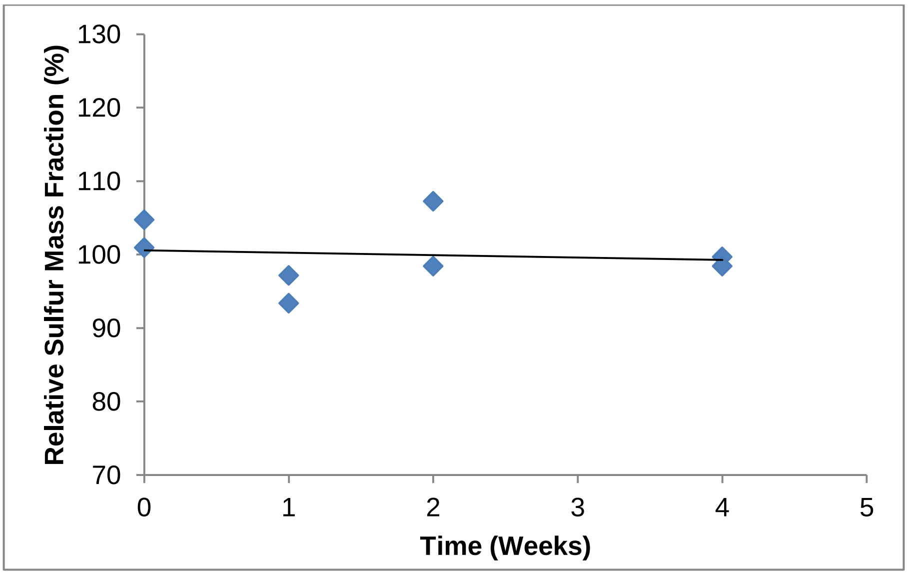

Figure 5. Graph for short term stability of UME CRM 1203-1 at 35 °C

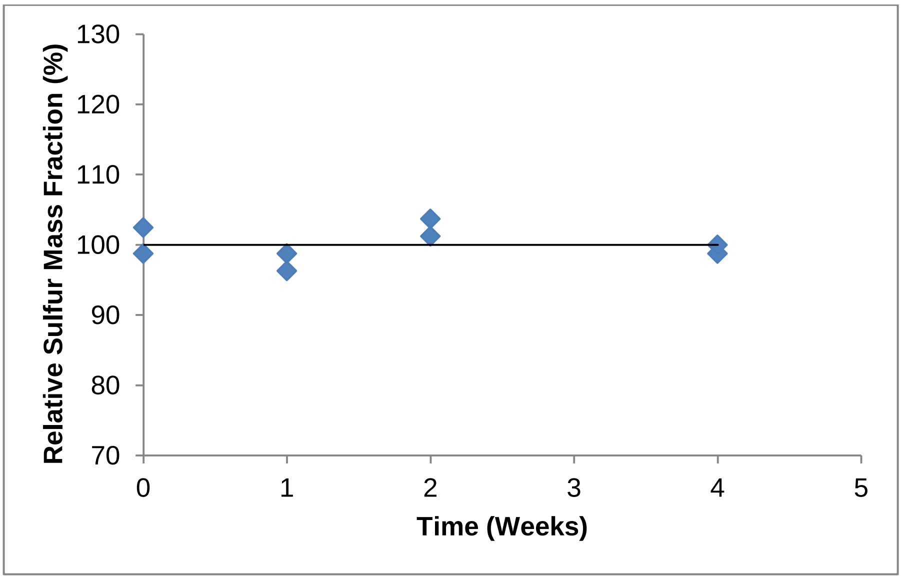

Figure 6. Graph for short term stability of UME CRM 1203-1 at 50 °C

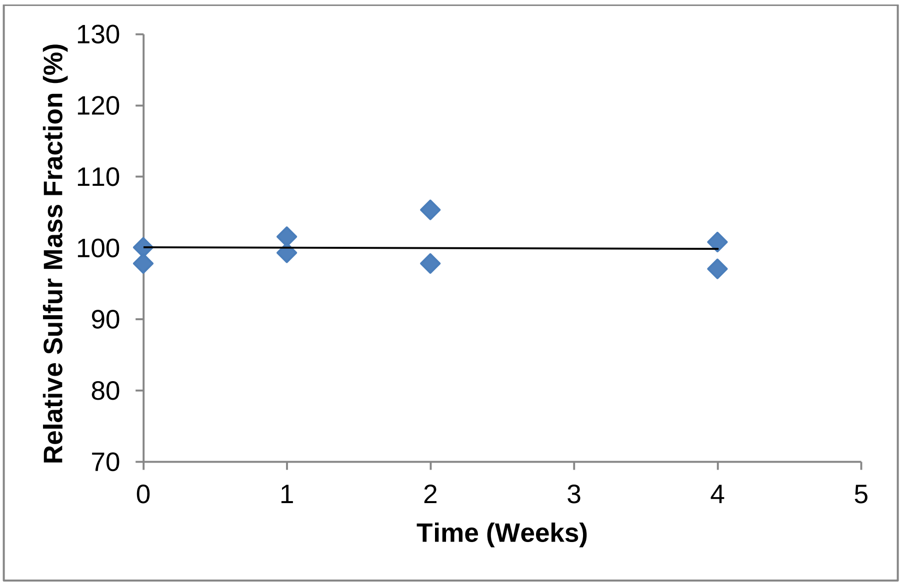

Figure 7. Graph for short term stability of UME CRM 1203-2 at 18 °C

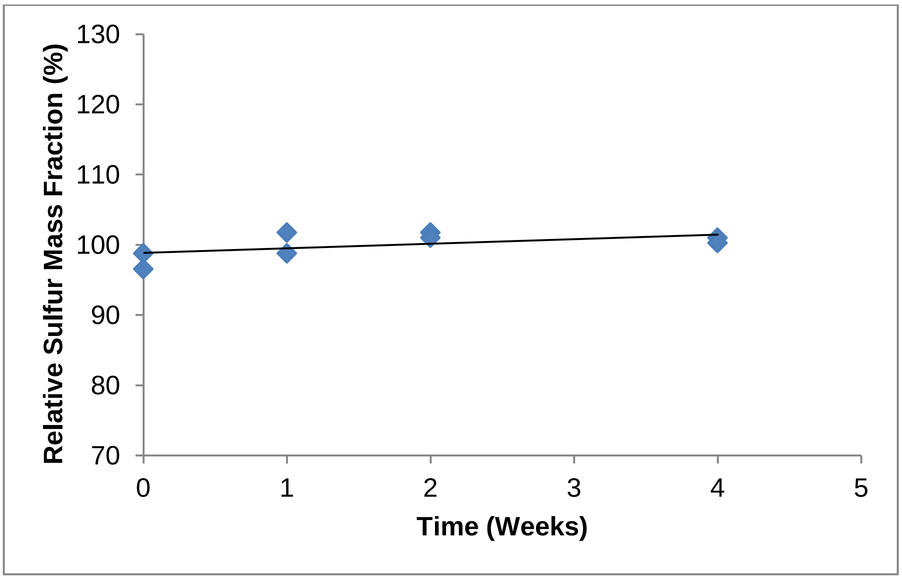

Figure 8. Graph for short term stability of UME CRM 1203-2 at 35 °C

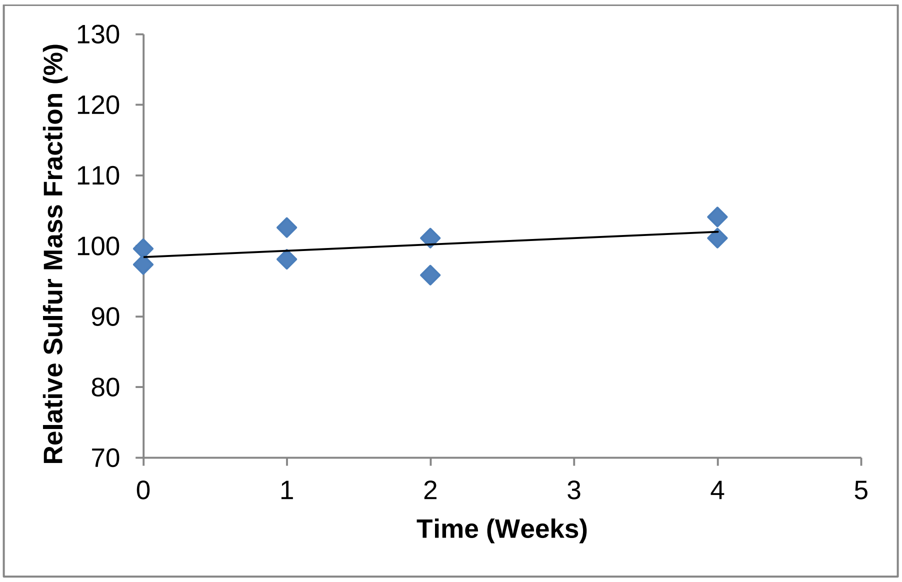

Figure 9. Graph for short term stability of UME CRM 1203-2 at 50 °C

Appendix 2. Plots for Long-Term Stability Study

Plots for the LTS study of UME CRM 1203-1 and UME CRM 1203-2 at 4 °C are given in Figure 10 and Figure 11, respectively.

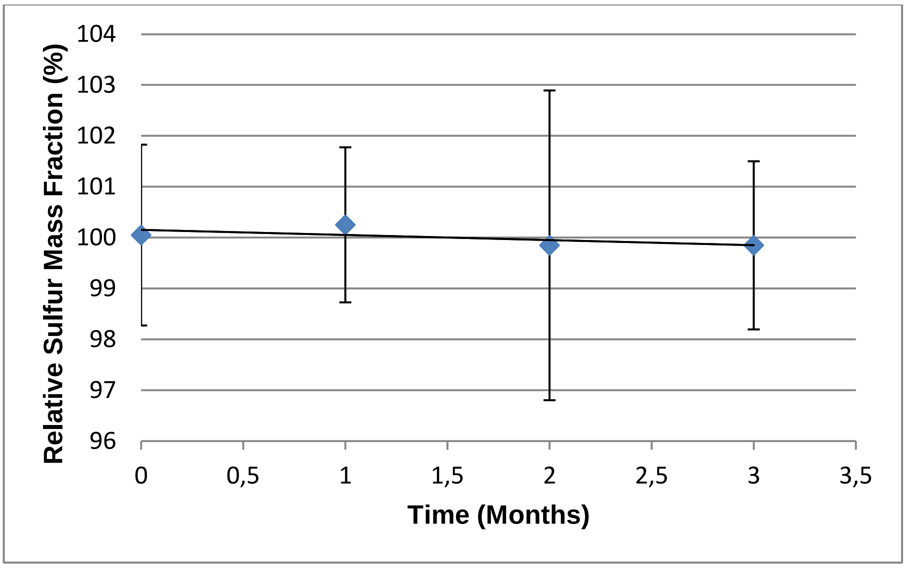

Figure 10. Graph for long term stability of UME CRM 1203-1 at 4 °C

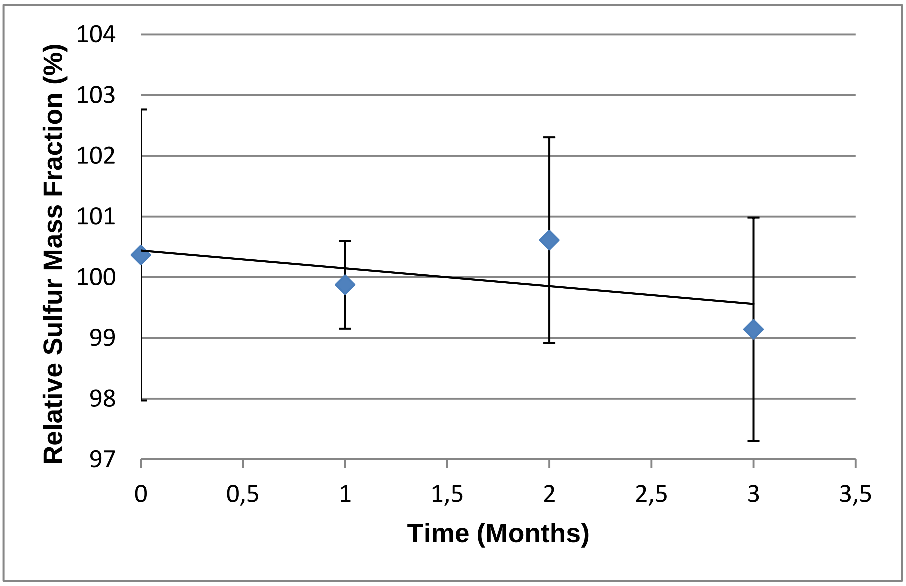

Figure 11. Graph for long term stability of UME CRM 1203-2 at 4 °C

Note: Error bars in Figures 10 and 11 show standard deviation of 6 replicate measurements.