

Colemanite  
Certified Reference Material  
UME CRM 1205

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### ABBREVIATIONS and SYMBOLS

|                   |   |
|-------------------|---|
| AAS               | Atomic Absorption Spectrometry  |
| ANOVA             | Analysis of Variance  |
| EMİGM             | Eti Maden İşletmeleri Genel Müdürlüğü   |
| FAAS              | Flame Atomic Absorption Spectrometry  |
| GFAAS             | Graphite Furnace Atomic Absorption Spectrometry   |
| HGAAS             | Hydride Generation Atomic Absorption Spectrometry   |
| GUM               | Guide to the expression of uncertainty in measurement                                     |
| HR-ICP-MS         | High Resolution Inductively Coupled Plasma Mass Spectrometry                              |
| ICP-MS            | Inductively Coupled Plasma Mass Spectrometry  |
| ID-ICP-MS         | Isotope Dilution Inductively Coupled Plasma Mass Spectrometry                             |
| ISO               | International Organization for Standardization  |
| STS               | Short Term Stability  |
| LTS               | Long Term Stability   |
| LOI               | Loss on Ignition  |
| $\alpha$          | Significance level  |
| $MS_{between}$    | Mean square between-units from ANOVA  |
| $MS_{within}$     | Mean square within-unit from ANOVA  |
| $n$               | Number of replicates per unit   |
| RSD               | Relative standard deviation   |
| $s$               | Standard deviation  |
| $S_{bb}$          | Between-units standard deviation (ANOVA)  |
| SGT               | Single Grubbs' Test   |
| SI                | International System of Units   |
| CRM               | Certified Reference Material  |
| $S_{wb}$          | Within-unit standard deviation (ANOVA)  |
| $S_{wb,rel}$      | Relative within-unit standard deviation   |
| $U_{bb}$          | Standard uncertainty related to possible between-unit heterogeneity                       |
| $U_{bb,rel}$      | Relative standard uncertainty related to possible between-unit 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 characterization  |
| $U_{char,rel}$    | Relative standard uncertainty related to characterization                                 |
| $U_{CRM}$         | Expanded uncertainty related to certified value   |
| $U_{CRM,rel}$     | Relative expanded uncertainty related to certified value                                  |
| $U_{lts}$         | 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                             |
| $V_{MS_{within}}$ | Degrees of freedom related to $MS_{within}$   |
| $k$               | Coverage factor   |
| $S_{bb,rel}$      | Relative between-bottle standard deviation  |

## ABSTRACT

This report describes the production process of UME CRM 1205 certified reference material, colemanite ( $2\text{CaO}\cdot 3\text{B}_2\text{O}_3\cdot 5\text{H}_2\text{O}$ , Dicalcium Hexaborate Pentahydrate) (CRM), in which aluminum (Al), arsenic (As), boron (B), calcium (Ca), iron (Fe), magnesium (Mg), sodium (Na), sulfur (S), silicon (Si), strontium (Sr) and Loss on Ignition (LOI) total mass fractions are certified. The process consists of material processing, homogeneity, short-term stability, characterization and long-term stability stages. The work was carried out in accordance with the requirements of ISO Guide 34: 2009 [1] and ISO Guide 35: 2006 [2].

The certificate values and the uncertainties related to these values have been calculated according to the "Guide to the expression of uncertainty in measurement" (GUM) [3].

The planning of the project, coordination of the activities and evaluation of the data were made by TÜBİTAK UME.

UME CRM 1205 certified reference material can be used by routine analysis and research laboratories that perform method development, validation studies and performance tests. Material can also be used to create quality control charts.

## INTRODUCTION

The use of CRM in chemical analysis plays an important role in ensuring the quality of measurement results and demonstrating their reliability. The certified chemical/physical properties are the values that have been agreed upon, and have been proven and published within the framework of certain criteria using scientific methods. A CRM in which the element content in colemanite matrix is certified is not available in the market as of the period of manufacture, and there is a lack in measurement in this field. Due to this deficiency, other CRMs that do not resemble the exact matrix are used in the analysis of colemanite samples. However, considering the importance of matrix effect in chemical analysis, it is known that the use of CRM whose matrix structure matches the samples is a priority to show the accuracy of the measurement results.

The mining, processing and utilization of boron mines, which are among the natural resources of Turkey, into products with high added value are among the national priorities. The ground form of colemanite, a boron ore, is produced by Eti Maden İşletmeleri Genel Müdürlüğü (EMİGM, Eti Mining Operations General Directorate) and is supplied to the market in line with certain quality standards. There is a need for certified reference material to be used in method development studies and in the quality control studies performed for the product and in the analysis of other products with high boron content. With the project, a material to meet these needs was produced.

During the production of the reference material, efforts have been made to certify the parameters that constitute the colemanite composition and are quality indicators for the product. In this context, the mass fraction of the elements Al, As, B, Ca, Fe, Mg, Na, S, Si and Sr and LOI have been certified in colemanite. Most of these elements constitute the matrix of colemanite ore with their oxide form and are certified at the % (w/w) level. The elements at lower levels, such as Al, As, Fe, Na and S, are certified on the mass fraction scale of milligrams per kilogram (mg/kg). The LOI parameter, which includes the sum of volatile substances such as water and organic structural components, has also been certified at % level by measurements with adapted and validated TS 3245 standard [4].

The certification process has been carried out by fulfilling the requirements based on ISO Guide 34 [1] and ISO Guide 35 [2] documents.

UME CRM 1205 Colemanite CRM produced by TÜBİTAK UME is intended to be used by laboratories measuring colemanite and similar samples as a quality assurance and quality control tool.

## PARTICIPANTS

The organizations involved in the raw material supply, processing, homogeneity, stability and characterization studies for CRM production and other activities of the project are given in Table 1.

**Table 1.** The participants contributed to the production and certification studies

| Action                                 | Participant  |
|--|--|
| Project management and data evaluation | TÜBİTAK Ulusal Metroloji Enstitüsü (UME), Gebze - Kocaeli, Turkey  |
| Raw material supply                    | Eti Maden İşletmeleri Genel Müdürlüğü (EMİGM), Teknoloji Geliştirme Daire Başkanlığı, Etimesgut - Ankara, Turkey |
| Processing                             | TÜBİTAK Ulusal Metroloji Enstitüsü (UME), Gebze - Kocaeli, Turkey  |
| Homogeneity Study                      | TÜBİTAK Ulusal Metroloji Enstitüsü (UME), Gebze - Kocaeli, Turkey  |
| Stability Studies                      | TÜBİTAK Ulusal Metroloji Enstitüsü (UME), Gebze - Kocaeli, Turkey  |
| Characterization Study                 | TÜBİTAK Ulusal Metroloji Enstitüsü (UME), Gebze - Kocaeli, Turkey  |

## MATERIAL PROCESSING

### Material supply

The sample chosen as candidate reference material was provided by EMİGM. Approximately 250 kg of ground raw material with a particle size of less than 75 µm, the commercial colemanite product, were obtained in packages of 25 kg each.

### Preparation stages, homogenization and bottling

Before starting the homogenization and bottling of the material, a suitable bottle and cap selection study was carried out. 125 mL amber colored glass bottles were preferred for the material and it was decided to use white, sealed polyethylene caps for these bottles. The glass bottles (Şişecam, Turkey) which were produced and packed under clean conditions (ISO Class 8) were visually inspected, and no powder or any other sign of contamination were found. Considering the levels of analytes targeted to be certified, it was decided that the bottles would not pose a contamination risk for the material and be used without any cleaning process.

For the homogenization process of powder raw material, approximately 210 kg of material was placed in a stainless steel 3D mixer tank. During this process, pure nitrogen gas was introduced into the tank and the contact of the sample with air and humidity was tried to be minimized. The tank after seal capped and screw fixed, was loaded into the 3D mixer (HKTM Megamix, Turkey). The homogenization process was carried out by allowing the material to mix for 4 hours. At the end of this period, the tank cover was opened under the air suction system and all the material was transferred to locked plastic bags using a plastic shovel. The sealed bags were placed in opaque polyethylene drums and the lid of the container was closed for minimizing the exposure to air, moisture and light until the batch was bottled.

The filling of the homogenized material was carried out with a semi-automatic filling device (Augapac, Belgium). The filling process started by transferring the material stored in sealed plastic bags to the filling chamber under nitrogen gas. The process, which continued by filling approximately 80 g of material in each bottle, continued until the filling of all the material was completed by continuously

feeding the filling chamber. After the bottles were filled, the cap was closed and the temporary label indicating the filling order was affixed, the outer surface was wiped and kept at room temperature. After filling all 2010 bottles, an automatic labeling machine (Farmatek, Turkey) was utilized for the permanent labeling following the filling order of bottles ("unit" hereinafter) and transferred to storage.

### **Natural levels**

The colemanite raw material was used as supplied by the manufacturer, and no additions were made for any of the certified parameters. Natural levels found in the material are certified.

### **Sterilization**

Since there is no risk of microbiological deterioration in the product, no sterilization process has been applied.

## **HOMOGENEITY**

For homogeneity study, 15 units are selected according to the stratified random sample selection principle. This ensures that the samples selected represent the total number of units. The homogeneity study was studied in two replicates from each unit for S element and three replicates for all other parameters. Homogeneity measurements were performed in random order using validated analytical methods to separate possible trends from filling and analytical sequence under repeatability conditions. Certified Reference Material (NIST SRM 1835) and blank sample analyzes were included in the measurement series to monitor possible contamination and the accuracy of the analysis. Element measurements were performed using Thermo Element 2 HR-ICP-MS (Bremen, Germany), Agilent 8800 QQQ ICP-MS (Hachioji, Japan) and Analytik Jena ZEE nit 700P (Jena, Germany). For LOI measurements, a muffle furnace (Protherm, Turkey) was used.

Mass fraction values obtained for each parameter as a result of the analysis were evaluated statistically by single-factor analysis of variance (ANOVA). In order to perform statistical evaluation with ANOVA, the data is expected to have a uniform distribution. For this purpose, the results obtained within and between units comparisons were checked for uniform distribution using histograms. Additionally, it was observed that the obtained data showed generally normal distribution by applying the Shapiro-Wilk test. As a result of these evaluations, it was determined that the distribution of the results (between units) obtained from the analysis of 15 units with 2 or 3 replicates per unit can be accepted as normal and uniform distribution for Al, Mg, S, Si and LOI. However, double-peak distribution was observed for the elements As, B, Ca, Fe, Na and Sr. The deviation from uniform distribution for these elements does not significantly affect the between-unit standard deviation estimate. In some elements, double-peak distributions were observed for some units, but the elements detected in these units were examined in more detail within the scope of characterization studies and no adverse effects were observed. The results obtained are presented in Table 2.

The data were checked and evaluated statistically for any trends and/or outliers arising from the analytical measurement sequence or the filling order of the units. In general, no trends were found for most parameters due to filling and the applied sequence during analysis. It was statistically determined that there was a trend for only B for the analysis order, but as a result of the examination of the data, it was seen that this determination did not occur in a linear manner throughout the analysis, so no

correction was applied for this situation. When the Grubbs' test is applied (one-way separately for maximum and minimum,  $\alpha = 0.05$ ), one outlier result was found for each of the elements As, B, Ca, Fe, Mg, Na and Sr. These outliers were retained for statistical analysis together with other values since no technical reason was found.

**Table 2.** Shapiro-Wilk test results for within-unit and between-units normal distribution\*

| Parameter | Within Unit |     |     |     |     |     |     |      |      |      |      |      |      |      |      | Between Units |
|-----------|-------------|-----|-----|-----|-----|-----|-----|------|------|------|------|------|------|------|------|---------------|
|           | 34          | 253 | 323 | 471 | 585 | 773 | 858 | 1060 | 1110 | 1322 | 1438 | 1505 | 1692 | 1764 | 1882 |               |
| Al        | +           | +   | +   | +   | +   | +   | +   | +    | +    | +    | +    | +    | +    | +    | +    | +             |
| As        | +           | +   | +   | +   | +   | -   | +   | +    | +    | +    | +    | +    | +    | +    | +    | -             |
| B         | +           | +   | +   | +   | -   | +   | +   | +    | +    | +    | +    | +    | +    | +    | +    | -             |
| Ca        | +           | +   | +   | +   | +   | +   | +   | +    | +    | +    | +    | +    | +    | -    | +    | -             |
| Fe        | +           | +   | +   | +   | +   | +   | -   | +    | +    | +    | +    | +    | +    | +    | +    | -             |
| Mg        | +           | +   | +   | +   | +   | +   | +   | +    | +    | +    | +    | +    | +    | -    | +    | +             |
| Na        | +           | +   | +   | +   | +   | +   | +   | +    | +    | +    | +    | +    | +    | -    | +    | -             |
| S         | +           | +   | +   | +   | +   | +   | +   | +    | +    | +    | +    | +    | +    | +    | +    | +             |
| Si        | +           | +   | +   | +   | +   | +   | +   | +    | +    | +    | +    | +    | +    | +    | +    | +             |
| Sr        | +           | -   | +   | +   | +   | +   | +   | +    | +    | +    | +    | +    | +    | +    | +    | -             |
| LOI       | +           | +   | +   | +   | +   | +   | +   | +    | +    | +    | +    | +    | +    | +    | +    | +             |

\*Plus sign shows the normal distribution whereas minus sign indicates that the distribution deviates from normal.

The following equation is applied to calculate the within-unit ( $s_{wb}$ ) and between-unit ( $s_{bb}$ ) standard deviation using ANOVA [5]:

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

where;

$MS_{within}$  : the mean of square of variance within the unit

$s_{wb}$  : standard deviation of the method as long as sub samples represent the whole unit.

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

In this equation,

$MS_{between}$  : Mean of square of variance between units,

$n$  : The number of replicates per unit.

When  $MS_{between}$  is found smaller than  $MS_{within}$ ,  $s_{bb}$  cannot be calculated. Instead,  $u_{bb}^*$ , heterogeneity obscured by method repeatability is given by the following equation:



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

Here,  $v_{MSwithin}$  is the degree of freedom for  $MS_{within}$ .

In the evaluations performed by applying ANOVA, the larger one of the values  $s_{bb}$  or  $u_{bb}^*$  was taken as the homogeneity uncertainty component  $u_{bb}$ . The results of the homogeneity study are given in Table 3.

**Table 3.** Results of the homogeneity assesment

| Parameter | Mean Value | Unit  | $s_{wb,rel}$ [%] | $s_{bb,rel}$ [%] | $u_{bb,rel}^*$ [%] | $u_{bb,rel}$ [%] |
|-----------|------------|-------|------------------|------------------|--------------------|------------------|
| Al        | 464        | mg/kg | 1.98             | -                | 0.58               | 0.58             |
| As        | 14.8       | mg/kg | 4.57             | 3.45             | 1.18               | 3.45             |
| B         | 12.3       | %     | 3.61             | 0.94             | 1.07               | 1.07             |
| Ca        | 20.4       | %     | 1.43             | -                | 0.42               | 0.42             |
| Fe        | 208        | mg/kg | 3.53             | 2.01             | 1.05               | 2.01             |
| Mg        | 1.18       | %     | 2.02             | -                | 0.60               | 0.60             |
| Na        | 297        | mg/kg | 2.16             | -                | 0.63               | 0.63             |
| S         | 795        | mg/kg | 1.24             | 0.23             | 0.53               | 0.53             |
| Si        | 1.90       | %     | 4.65             | -                | 1.37               | 1.37             |
| Sr        | 0.60       | %     | 1.93             | -                | 0.57               | 0.57             |
| LOI       | 24.9       | %     | 0.14             | -                | 0.12               | 0.12             |

Even when outliers are not discarded and included in the statistical calculation, the between-unit variation for most elements is generally lower than the target maximum value. The homogeneity uncertainty values for the candidate CRM remained below the highest target uncertainty value ( $\leq 3\%$ ), except As.

In the measurements of B, Ca, Mg and Sr, it was observed that one of the repeated measurements of a unit (# 253) did not come through with the others as a result of instrument error. The measurement of this sample was repeated and it was seen that there was no effect to change the uncertainty value of homogeneity. The data of this unit is not included in the calculations.

All data used for homogeneity assessment are given in Annex 1.

### **Minimum sample intake**

Since homogeneity was achieved through a technically valid set of results accepted for characterization, no special study was required for the minimum sampling. It was decided to use 0.10 g sample amount for the elements and 1.0 g sample amount for LOI parameter as the minimum sampling amount to represent the whole unit used in characterization studies.

### **STABILITY**

Stability studies are carried out in the laboratory by simulating environmental conditions during the delivery of the material to the customer (short-term stability, STS) and storage conditions (long-term stability, LTS). For a geological material colemanite, it is considered that there is no risk of instability as long as there is no external intervention and the recommended transportation and storage conditions are met in the short and long term. Since the oxide forms of the elements, which are the main components, are stable forms, they are not expected to undergo any degradation over time or to transform into different molecular structures by chemical reaction to change the composition. However, tests were still carried out to prove the stability as a requirement of the CRM production process.

Fourteen units selected for short term stability test and 8 units selected for long term stability test were determined by random stratified sample selection principle.

For short term stability study, the test temperatures were determined as +40 °C and +60 °C and the test periods as 1, 2 and 4 weeks. For each time interval to be tested at both temperatures, 2 units were placed in the test cabinet. In the stability test, 2 units were allocated for the reference point and these units were placed directly at the reference temperature, +18 °C. At the end of each test period, 2 units from both temperature conditions were transferred to the reference temperature. When the four-week test period was completed, all units transferred and the units served at the reference were analyzed simultaneously.

For long term stability test, 8 units has been stored at  $(18 \pm 2)$  °C for 0, 2, 4 and 6 months. At the end of the test period, the units were moved from 18 °C to -20 °C, and all bottles transferred to the reference temperature were analyzed at the same time (isochronous) with the bottles kept at -20 °C for reference.

### **Short Term Stability Study**

Simultaneous measurement results were first grouped according to the time points and evaluated for each time point. These evaluations were carried out for both temperatures separately.

Values at each point were analyzed for outliers at 95% and 99% confidence levels using the Grubbs' test. The calculated values for each time point were plotted against time. The relationship between the variables was analyzed to determine whether there was any significant change in mass fraction and loss on ignition values in time (regression analysis). The calculated slopes were tested for significance using the *t*-test. Here,  $t_{\alpha,df}$  were used as two-tailed critical *t* value for  $\alpha = 0.05$  (95% confidence level) significance level. Related graphics are given in Annex 2.

In the statistical evaluations of the obtained data (Grubbs' test), the presence of outliers for Al (40 °C), As (40 °C), Na (40 °C) and S (40 °C) were determined. Observing that the outliers occur in the measurement made from the same unit for all detected parameters strengthens the possibility of a

measurement-related error. In addition, the fact that the test results performed at 60 °C for these parameters do not indicate the presence of any outlier supports the assumption that the observed inconsistency is a measurement cause. However, these values were kept among the data without discarding. It has been shown that no deviation was encountered by statistical evaluations even when the outliers were retained. The trend line was drawn for the evaluation of the presence of correlation among the mass fraction data drawn against the test time. It was determined that the slopes of the plotted graphics were not significantly different from zero for almost all of the parameters as a result of the applied *t*-test. The data evaluation results of the short-term stability studies performed at +40 °C and +60 °C are given in Table 4.

As a result of the evaluation, it was seen that the parameters to be certified in the certified reference material produced were stable at all temperatures (+40 °C and +60 °C) for at least 4 weeks, despite the presence of some outliers. As a result, samples can be delivered to the end user without any cooling application, provided that the temperature does not exceed +60 °C and the time does not exceed 1 week.

**Table 4.** Short-term stability test results

| Parameter | Is the slope of the graph plotted for 40 °C significantly different from zero at the 95% confidence level? | Number of outliers at 95% confidence level* | Is the slope of the graph plotted for 60 °C significantly different from zero at the 95% confidence level? | Number of outliers at 95% confidence level* |
|-----------|--|---|--|---|
| Al        | No   | 1   | No   | -   |
| As        | No   | 1   | No   | -   |
| B         | No   | -   | No   | -   |
| Ca        | No   | -   | Yes  | -   |
| Fe        | Yes  | -   | No   | -   |
| Mg        | No   | -   | No   | -   |
| Na        | No   | 1   | No   | -   |
| S         | No   | 1   | No   | -   |
| Si        | No   | -   | No   | -   |
| Sr        | No   | -   | No   | -   |
| LOI       | No   | -   | No   | -   |

\*SGT: Single Grubbs' Test result

### Long Term Stability Study

The shelf life of the produced CRMs is determined according to the results of long-term stability studies. As mentioned above, long-term stability measurements were performed using two units for each time point and three independent samplings from each unit. This study is designed to cover a period of 6 months. At the end of the specified test period, the samples taken from the test temperature (18 ± 2) °C were transferred to -20 °C and at the end of 6 months the analyzes were performed simultaneously. Two units designated as reference were stored at -20 °C.

Three replicate results were obtained from each selected unit for each time point. The results and graphics obtained at each point are given in Annex 3. The error lines at each time point were calculated as the standard deviation of the three results obtained for each of the two units.

Among the obtained data, the one-sided Grubbs' test was applied to examine whether there was an outlier at 95% and 99% confidence intervals. For the elements As, Ca, Fe and Mg, outliers at 95% confidence interval were determined. Since there were no technical reasons to discard, all the data including the detected outliers were retained in the assessment.

The values found were analyzed by drawing the concordance line (regression line) in the graph of concentration versus time. The uncertainty value of the certified reference material due to long-term stability is calculated using equation (4) [6].

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

Here,

*RSD* : Relative standard deviation of all the measurement results,

$t_i$  : Time point for each test repeat,

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

$t$  : Suggested shelf life for 18 °C.

Shelf life has been determined as 12 months for the contribution of uncertainty arising from long-term stability to total uncertainty. As the storage temperature, although the tests are carried out at 18 ° C, laboratory ambient temperature is recommended for practical reasons. Long-term stability is one of the four parameters that contribute to the total uncertainty. Results calculated in this way are given in Table 5 and graphics are given in Annex 3.

In addition, reassessments will be made at certain intervals based on the results of regular post-certification monitoring to ensure stability beyond the specified shelf life.

**Table 5.** Long-term stability test results

| Parameter | $u_{Its,rel}$ % (12 months) |
|-----------|-----------------------------|
| Al        | 1.66                        |
| As        | 0.92                        |
| B         | 1.17                        |
| Ca        | 0.87                        |
| Fe        | 2.18                        |
| Mg        | 1.58                        |
| Na        | 1.64                        |
| S         | 4.05                        |
| Si        | 3.28                        |
| Sr        | 1.47                        |
| LOI       | 1.25                        |

## CHARACTERIZATION

Based on ISO Guide 34, characterization can be done with four different approaches [1]. In this project, characterization was done by applying two of these defined approaches: i) *using primary measurement method* and ii) *two or more independent reference methods applied by one laboratory*. The characterization of B, S and Sr were performed by ID-ICP-MS, a potential primary measurement technique. The results were validated using HR-ICP-MS method (matrix matched external calibration) for verification. Although the ID-ICP-MS method is primarily used for iron, a second technique (ICP-MS) has been validated and the results are given as the average of both techniques. The characterization of Al, As, Ca, Mg, Na and Si was performed by using two independent reference methods. In this context, ICP-MS and AAS (Atomic Absorption Spectrometry) techniques were used for the characterization of Al, As, Ca, Mg, Na and Si. For AAS measurements, methods for Graphite Furnace AAS (GFAAS) for Al, Hydride Generation AAS (HGAAS) for As and Flame AAS (FAAS) for Ca, Mg, Na and Si were developed and applied.

Characterization studies for LOI value were carried out by using gravimetry method applied as a primary level method. The measurement value is expressed as the mass loss by the ignition of samples at 950 °C in accordance with the recommendations specified in the TS 3245 standard. Measurements were carried out using 1.0 g of material.

All certified parameters and techniques used in characterization studies for these parameters are given in Table 6.

**Table 6.** Techniques used in characterization studies

| Parameter | Technique |        |      |       |       |            |
|-----------|-----------|--------|------|-------|-------|------------|
|           | ID-ICP-MS | ICP-MS | FAAS | GFAAS | HGAAS | Gravimetry |
| Al        |           | +      |      | +     |       |            |
| As        |           | +      |      |       | +     |            |
| B         | +         |        |      |       |       |            |
| Ca        |           | +      | +    |       |       |            |
| Fe        | +         | +      |      |       |       |            |
| Mg        |           | +      | +    |       |       |            |
| Na        |           | +      | +    |       |       |            |
| S         | +         |        |      |       |       |            |
| Si        |           | +      | +    |       |       |            |
| Sr        | +         |        |      |       |       |            |
| LOI       |           |        |      |       |       | +          |

For each method applied in characterization studies, 2 units previously reserved for this purpose were used. In ICP-MS, FAAS, GFAAS and HGAAS measurements, at least three subsamples were prepared

from each unit on two different days (including different calibration curves and sample dissolving and preparation) and a total of 6 independent results were produced. In the characterization study performed with the ID-ICP-MS method, the measurements were completed on the same day. In total, at least 6 independent results from two units for each element were generated in ID-ICP-MS measurements. LOI measurements were performed on 4 different days by producing 4 independent results from both units.

### PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT

For each element, assignment of property values and uncertainty values were performed considering the characterization strategy followed, measurement results and associated uncertainties, and the uncertainty contributions from homogeneity and stability measurements.

The property value of the elements (B, S and Sr) characterized by primary measurement method ID-ICP-MS was the average of independent results. The property value for Fe was taken as the arithmetic mean of the value obtained from the ID-ICP-MS study and the value obtained from the ICP-MS measurements. Uncertainty values estimated using bottom-up approach were taken into account as  $U_{char}$ .

The value assignment of the elements (Al, As, Ca, Fe, Mg, Na and Si), of which characterization studies were performed using two reference methods approach, were carried out by unweighted mean of the results obtained by each method. The uncertainty value,  $U_{char}$ , were determined by merging the uncertainty values obtained for each method.

The uncertainty component of the certified value is composed of the uncertainty contributions from the characterization study ( $u_{char}$ ), the homogeneity study ( $u_{bb}$ ), the short-term stability study ( $u_{sts}$ ) and the long-term stability study ( $u_{lts}$ ). The uncertainty of the CRM were determined by combining the components affecting value of the assigned uncertainty are calculated using the following equation:

$$U_{CRM} = k \sqrt{u_{char}^2 + u_{bb}^2 + u_{sts}^2 + u_{lts}^2} \quad (5)$$

Certified values and associated uncertainties are given in Table 7.

**Table 7.** Certified values and uncertainties

| Parameter | Certified Value,<br>% | Uncertainty,<br>% | Parameter | Certified Value,<br>mg/kg | Uncertainty,<br>mg/kg |
|-----------|-----------------------|-------------------|-----------|---------------------------|-----------------------|
| B         | 12.2                  | 0.6               | Al        | 448                       | 43                    |
| Ca        | 20.2                  | 0.7               | As        | 14,8                      | 1,8                   |
| Mg        | 1.10                  | 0.06              | Fe        | 215                       | 29                    |
| Si        | 2.01                  | 0.13              | Na        | 290                       | 24                    |
| Sr        | 0.59                  | 0.02              | S         | 780                       | 40                    |
| LOI       | 24.7                  | 0.7               |           |                           |                       |

## TRACEABILITY

Providing metrological traceability for the characterization values of the CRM is possible by using calibration standards traceable to SI units. All measurements made with the external calibration method were performed using NIST SRM 3100 series single element calibration solutions. For the measurements made with the ID-ICP-MS method, certified reference materials enriched in traceable isotopes were used. If these are not found, traceability are based on NIST SRM 3100 series with the Triple-IDMS method.

The methods used in the analysis have been validated. NIST SRM 1835 "Borate Ore" matrix certified reference material was used to control the accuracy of the analysis. As a result of the comparison between the values found and the certificate values, it was observed that there was no significant deviation. The recovery rates for the arsenic were determined by adding a standard over the test sample and by using the NIST SRM 2711a "Montana Soil" certified reference material.

Loss on ignition measurements were carried out using gravimetry method in accordance with the requirements of TS 3245 standard for the specified sampling amount. The balances used in weighing were calibrated by TÜBİTAK UME and their traceability to SI units was provided. The accuracy of the method has been checked using NIST SRM 1835 and has been validated.

## INSTRUCTION FOR USE

### Storage Conditions

The material should be stored at ordinary laboratory temperatures. TÜBİTAK UME cannot be held responsible for changes that might happen to the material at customer's premises due to noncompliance with the instructions for use, and the given storage conditions.

### Safety Information

The material is for laboratory use only. Usual laboratory precautions apply during storage and usage. It is strongly recommended that the material must be handled and disposed according to the safety guidelines where applicable. Users are recommended to avoid inhalation of the powder material, and work under proper ventilation. Please refer to the Safety Datasheet before any use of the material.

### Intended Use

This material is intended to be used for method validation of the determination of element mass fractions and loss on ignition in colemanite and quality control purposes.

### Instructions for Use

The bottle must be shaken before opening for assurance of homogeneity. All precautions must be taken in order to prevent contamination and moisture uptake.

### Minimum Sample Intake

Minimum sample intake is 0.10 g for elements, and is 1.0 g for loss on ignition measurements.

### Using Certificate Values

In order to evaluate the method performance, the measured values of the CRM are compared with the certificate values [7]. The comparison process can be summarized as follows:

- Absolute difference between the average value found and the certificate value ( $\Delta_m$ )
- Standard uncertainty of measurement ( $u_{meas}$ ) and standard uncertainty in certificate value ( $u_{CRM}$ ) are combined,

$$u_{\Delta} = \sqrt{u_{meas}^2 + u_{CRM}^2}$$

- The combined uncertainty is multiplied by the coverage factor ( $k = 2$ ) to calculate the expanded uncertainty, which corresponds to a 95% confidence level.

$$U_{\Delta} = 2 \times u_{\Delta}$$

If  $\Delta_m \leq U_{\Delta}$ , it is assumed that there is no significant difference between the measurement result and the certificate value at 95% confidence level.

### ACKNOWLEDGEMENTS

We would like to thank Mine Bilsel, Dr. T. Eriñç Engin, Dr. Kevser Topal for their contribution as technical evaluation committee member, and Gökhan Aktaş, Hatice Altuntaş and Elif Turan who took part in the processing of the material. We would like to express our gratitude to Hasibe Yılmaz, who contributed to the physical characterization studies of the material, and to our interns Mirlan Alimbekov and Ceren Köseođlu, who contributed to LOI measurements.

We would like to thank Eti Mining Operations General Directorate, Technology Development Department and their officials who brought this CRM production project to our attention and made it possible to realize it with financial support.

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- [1] ISO Guide 34:2009, General requirements for the competence of reference materials producers
- [2] ISO Guide 35:2006, Reference materials – General and statistical principles for certification
- [3] Evaluation of uncertainty in measurement - Guide to the expression of uncertainty in measurement, JCGM 100:2008
- [4] TS 3245, Methods for the Analysis of Ceramic Whiteware Clays - Determination of Moisture and Loss on Ignition Contents, 1978
- [5] T. P. J. Linsinger, J. Pauwels, A. M. H. Van der Veen, H. Schimmel, A. Lamberty, Homogeneity and stability of reference materials, Accred. Qual. Assur. 6 (2001) 20 - 25.
- [6] T. P. J. Linsinger, J. Pauwels, A. Lamberty, H. Schimmel, A. M. H. van der Veen, L. Siekmann, Estimating the uncertainty of stability for matrix CRMs, Fresenius J Anal Chem 370 (2001) 183 - 188.
- [7] [http://www.ermcrm.org/html/ERM\\_products/application\\_notes/application\\_note\\_1/application\\_note\\_1\\_english\\_en.pdf](http://www.ermcrm.org/html/ERM_products/application_notes/application_note_1/application_note_1_english_en.pdf) (22/03/2010).



**REVISION HISTORY**

| Date       | Remark  |
|------------|---|
| 26.12.2017 | First Publication.  |
| 27.02.2018 | LOI parameter recertified using an in-house method adapted from TS 3245 standard, and the uncertainties were updated. Sulfur (S) certified value was updated. |

### Annex 1. Data for Homogeneity Study

**Table A1.1.** UME CRM 1205 homogeneity data for Al, As, B and Ca

| Unit        | Al (mg/kg) |     |     | As (mg/kg) |      |      | B (%) |      |      | Ca (%) |      |      |
|-------------|------------|-----|-----|------------|------|------|-------|------|------|--------|------|------|
|             | T1         | T2  | T3  | T1         | T2   | T3   | T1    | T2   | T3   | T1     | T2   | T3   |
| <b>34</b>   | 467        | 467 | 457 | 15.6       | 15.0 | 14.6 | 12.1  | 11.9 | 11.9 | 20.2   | 20.3 | 20.3 |
| <b>253</b>  | 450        | 468 | 449 | 15.4       | 14.7 | 14.7 | 11.8  | -*   | 11.9 | 20.3   | -*   | 20.2 |
| <b>323</b>  | 446        | 463 | 452 | 14.6       | 15.3 | 14.9 | 11.9  | 11.9 | 12.1 | 20.4   | 20.5 | 20.4 |
| <b>471</b>  | 456        | 447 | 461 | 13.0       | 13.0 | 13.3 | 12.4  | 11.7 | 11.9 | 20.3   | 20.1 | 20.3 |
| <b>585</b>  | 454        | 457 | 458 | 15.7       | 13.1 | 14.4 | 11.2  | 11.8 | 10.1 | 20.4   | 20.4 | 20.7 |
| <b>773</b>  | 455        | 447 | 467 | 13.4       | 12.5 | 15.6 | 11.8  | 11.5 | 12.2 | 20.2   | 20.4 | 20.7 |
| <b>858</b>  | 465        | 456 | 463 | 15.1       | 14.9 | 15.4 | 11.9  | 11.5 | 11.7 | 20.4   | 20.3 | 20.4 |
| <b>1060</b> | 448        | 445 | 457 | 15.6       | 14.9 | 15.5 | 11.8  | 11.1 | 11.5 | 20.2   | 20.5 | 20.5 |
| <b>1110</b> | 442        | 462 | 479 | 14.8       | 15.2 | 15.5 | 12.3  | 12.2 | 11.7 | 20.4   | 20.7 | 20.5 |
| <b>1322</b> | 475        | 453 | 443 | 14.5       | 15.2 | 15.2 | 11.9  | 11.4 | 12.2 | 20.2   | 20.5 | 20.7 |
| <b>1438</b> | 465        | 468 | 454 | 14.8       | 14.8 | 14.8 | 11.8  | 12.1 | 12.0 | 20.9   | 20.3 | 20.2 |
| <b>1505</b> | 448        | 446 | 450 | 15.2       | 15.0 | 15.3 | 12.2  | 11.5 | 11.8 | 20.6   | 20.2 | 20.4 |
| <b>1692</b> | 457        | 460 | 461 | 15.1       | 15.1 | 14.8 | 12.0  | 11.0 | 11.9 | 20.4   | 20.7 | 20.4 |
| <b>1764</b> | 452        | 459 | 469 | 15.4       | 15.9 | 15.0 | 11.9  | 12.2 | 11.7 | 20.4   | 20.5 | 18.9 |
| <b>1882</b> | 459        | 450 | 442 | 15.0       | 14.8 | 14.9 | 12.2  | 11.8 | 11.7 | 20.3   | 20.4 | 20.2 |

\* Not measured

**Table A1.2.** UME CRM 1205 homogeneity data for Fe, Mg, Na and S

| Unit        | Fe (mg/kg) |     |     | Mg (%) |      |      | Na (mg/kg) |     |     | S (mg/kg) |     |     |
|-------------|------------|-----|-----|--------|------|------|------------|-----|-----|-----------|-----|-----|
|             | T1         | T2  | T3  | T1     | T2   | T3   | T1         | T2  | T3  | T1        | T2  | T3  |
| <b>34</b>   | 215        | 214 | 221 | 1.16   | 1.18 | 1.19 | 305        | 295 | 289 | 794       | 788 | 759 |
| <b>253</b>  | 197        | 208 | 211 | 1.18   | -*   | 1.16 | 289        | 297 | 291 | 705       | 715 | 698 |
| <b>323</b>  | 199        | 196 | 203 | 1.19   | 1.20 | 1.20 | 288        | 301 | 296 | 692       | 775 | 789 |
| <b>471</b>  | 213        | 191 | 213 | 1.17   | 1.17 | 1.21 | 294        | 286 | 295 | 710       | 637 | 655 |
| <b>585</b>  | 198        | 198 | 197 | 1.19   | 1.19 | 1.18 | 293        | 303 | 296 | 643       | 618 | 625 |
| <b>773</b>  | 202        | 199 | 206 | 1.16   | 1.20 | 1.20 | 298        | 292 | 295 | 698       | 717 | 825 |
| <b>858</b>  | 205        | 297 | 198 | 1.20   | 1.17 | 1.18 | 294        | 293 | 305 | 786       | 709 | 697 |
| <b>1060</b> | 219        | 216 | 209 | 1.16   | 1.21 | 1.21 | 300        | 288 | 302 | 758       | 767 | 721 |
| <b>1110</b> | 202        | 217 | 210 | 1.18   | 1.20 | 1.18 | 289        | 304 | 316 | 743       | 828 | 855 |
| <b>1322</b> | 277        | 221 | 204 | 1.16   | 1.19 | 1.21 | 302        | 302 | 295 | 841       | 848 | 777 |
| <b>1438</b> | 205        | 217 | 217 | 1.22   | 1.15 | 1.17 | 297        | 306 | 297 | 714       | 726 | 782 |
| <b>1505</b> | 221        | 200 | 213 | 1.19   | 1.16 | 1.19 | 291        | 291 | 299 | 777       | 824 | 818 |
| <b>1692</b> | 207        | 208 | 205 | 1.19   | 1.22 | 1.19 | 308        | 298 | 304 | 809       | 797 | 750 |
| <b>1764</b> | 222        | 217 | 207 | 1.18   | 1.22 | 1.12 | 293        | 296 | 303 | 724       | 722 | 788 |
| <b>1882</b> | 209        | 224 | 204 | 1.17   | 1.19 | 1.16 | 302        | 302 | 292 | 852       | 848 | 811 |

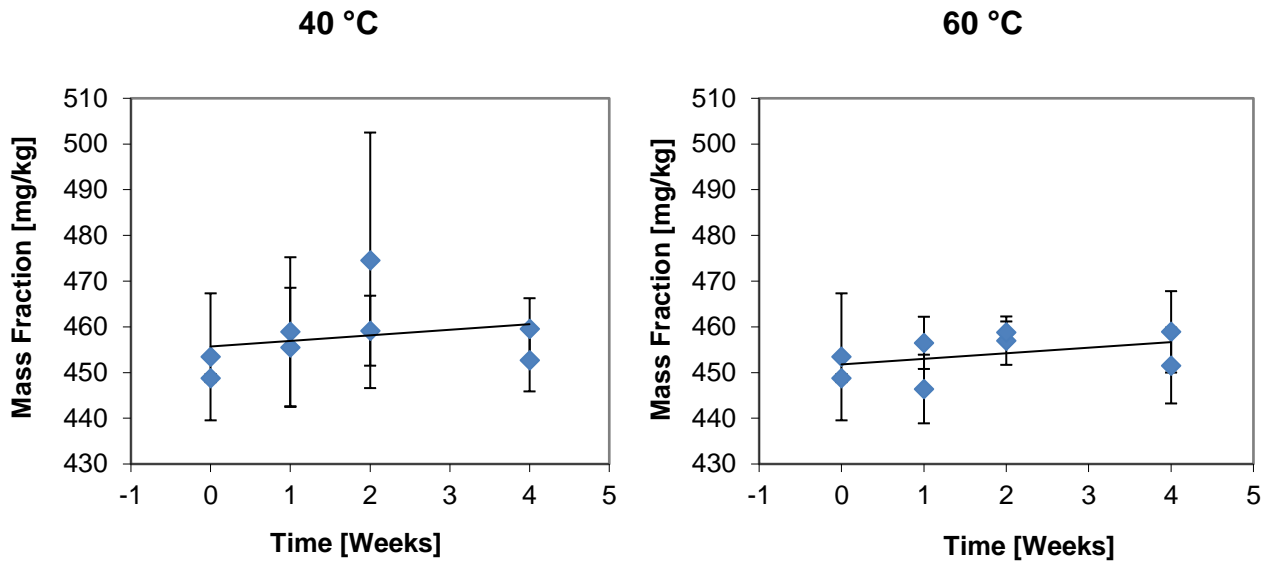
\* Not measured

**Table A1.3.** UME CRM 1205 homogeneity data for Si, Sr and LOI

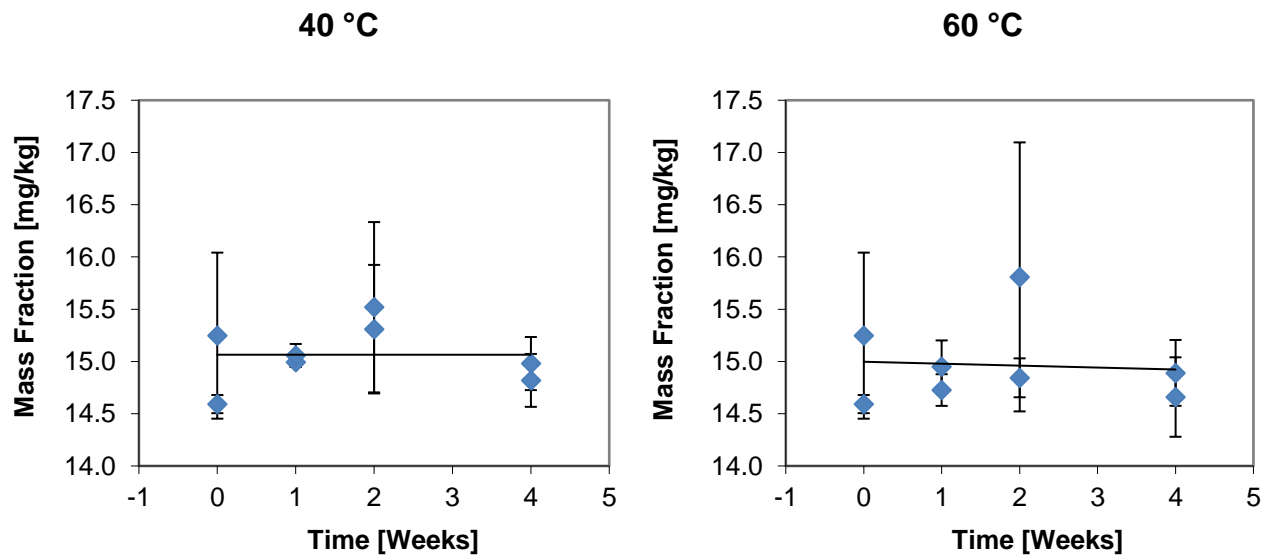
| Unit        | Si (%) |      |      | Sr (%) |       |       | LOI (%) |       |       |
|-------------|--------|------|------|--------|-------|-------|---------|-------|-------|
|             | T1     | T2   | T3   | T1     | T2    | T3    | T1      | T2    | T3    |
| <b>34</b>   | 1.85   | 1.86 | 1.88 | 0.592  | 0.603 | 0.592 | 24.96   | 24.84 | 24.92 |
| <b>253</b>  | 1.85   | 1.84 | 1.79 | 0.596  | -*    | 0.586 | 25.01   | 24.76 | 25.05 |
| <b>323</b>  | 2.12   | 1.75 | 1.88 | 0.594  | 0.595 | 0.598 | 25.00   | 24.95 | 25.11 |
| <b>471</b>  | 2.01   | 1.81 | 1.95 | 0.593  | 0.592 | 0.597 | 25.01   | 24.89 | 24.91 |
| <b>585</b>  | 1.91   | 1.78 | 2.02 | 0.584  | 0.597 | 0.597 | 24.89   | 25.00 | 24.94 |
| <b>773</b>  | 1.85   | 2.06 | 2.10 | 0.595  | 0.589 | 0.602 | 24.77   | 24.96 | 24.94 |
| <b>858</b>  | 1.79   | 1.98 | 1.92 | 0.590  | 0.594 | 0.595 | 24.98   | 24.83 | 24.90 |
| <b>1060</b> | 1.82   | 1.89 | 1.91 | 0.602  | 0.596 | 0.600 | 25.00   | 24.85 | 24.98 |
| <b>1110</b> | 1.91   | 1.91 | 1.87 | 0.590  | 0.602 | 0.594 | 24.97   | 24.88 | 25.21 |
| <b>1322</b> | 1.89   | 1.84 | 1.93 | 0.594  | 0.595 | 0.593 | 24.99   | 24.94 | 25.02 |
| <b>1438</b> | 1.95   | 1.77 | 1.97 | 0.619  | 0.594 | 0.601 | 25.19   | 24.83 | 24.86 |
| <b>1505</b> | 1.85   | 1.82 | 1.83 | 0.596  | 0.602 | 0.599 | 24.94   | 24.83 | 24.86 |
| <b>1692</b> | 1.94   | 1.88 | 1.90 | 0.589  | 0.601 | 0.598 | 25.00   | 24.88 | 25.11 |
| <b>1764</b> | 1.84   | 1.99 | 1.96 | 0.601  | 0.607 | 0.538 | 24.97   | 24.92 | 24.86 |
| <b>1882</b> | 1.97   | 1.90 | 1.87 | 0.593  | 0.595 | 0.594 | 24.97   | 24.84 | 24.96 |

\* Not measured

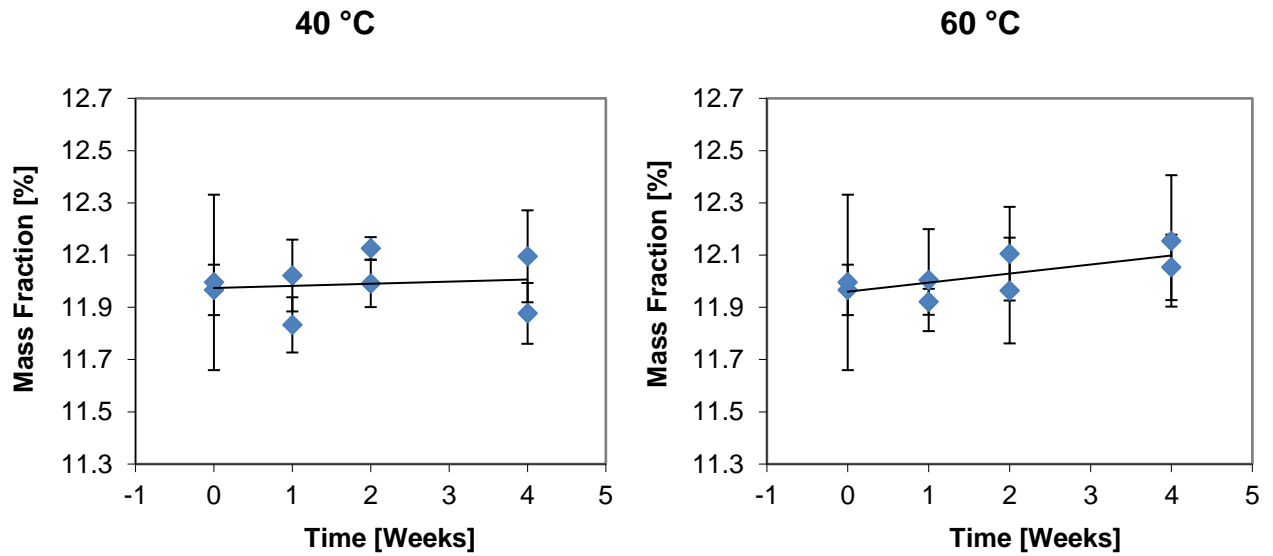
### Annex 2. The Graphs for Short-Term Stability



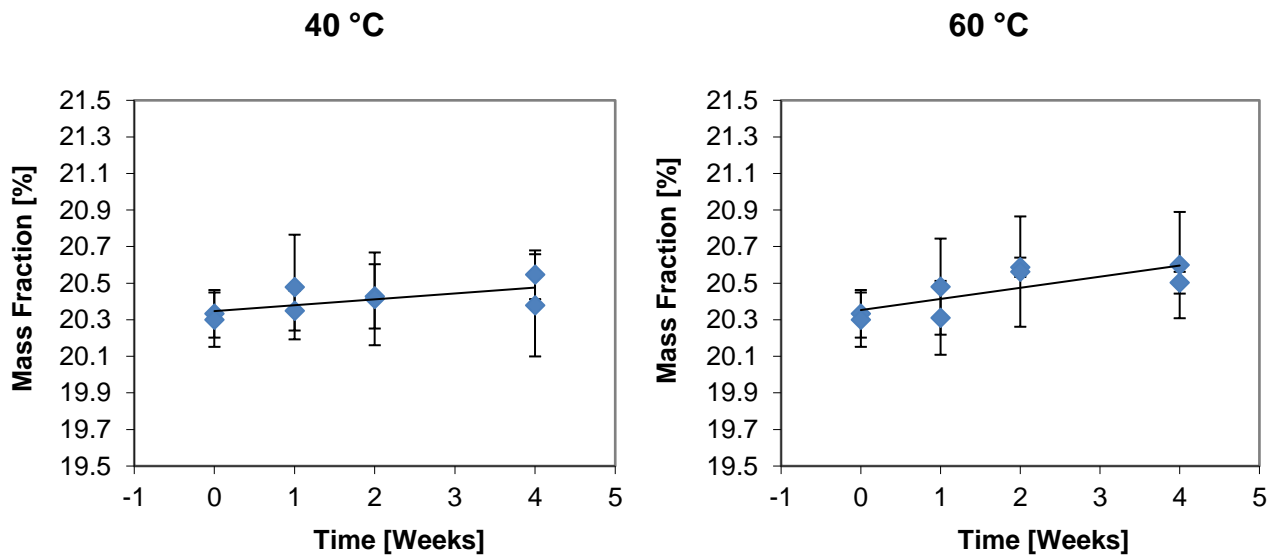
**Figure A2.1.** UME CRM 1205 short-term stability graphs for Al



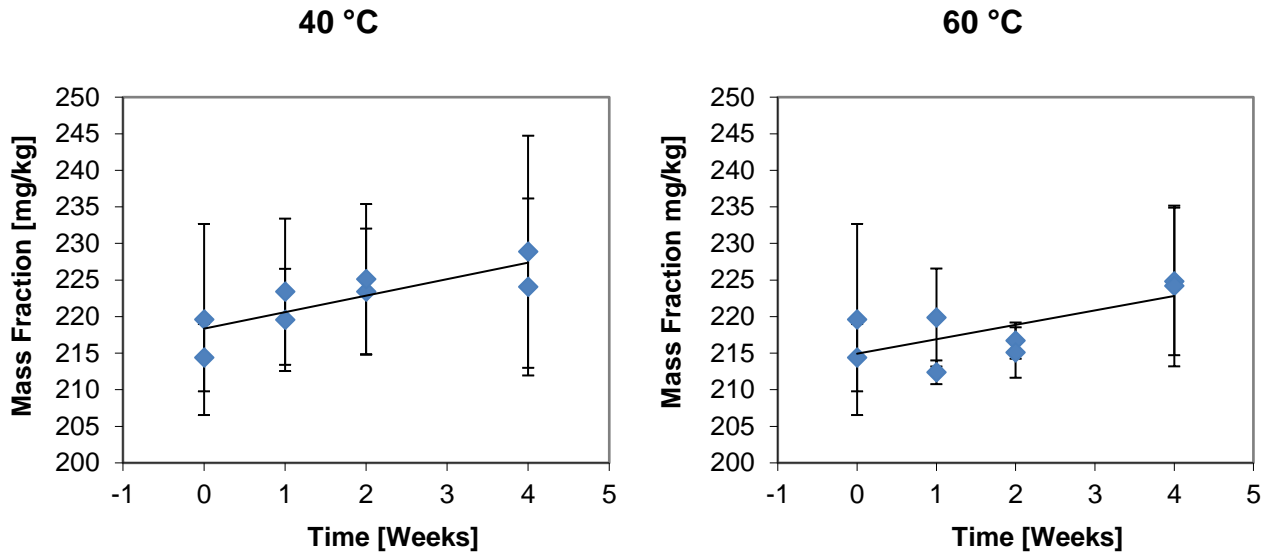
**Figure A2.2.** UME CRM 1205 short-term stability graphs for As



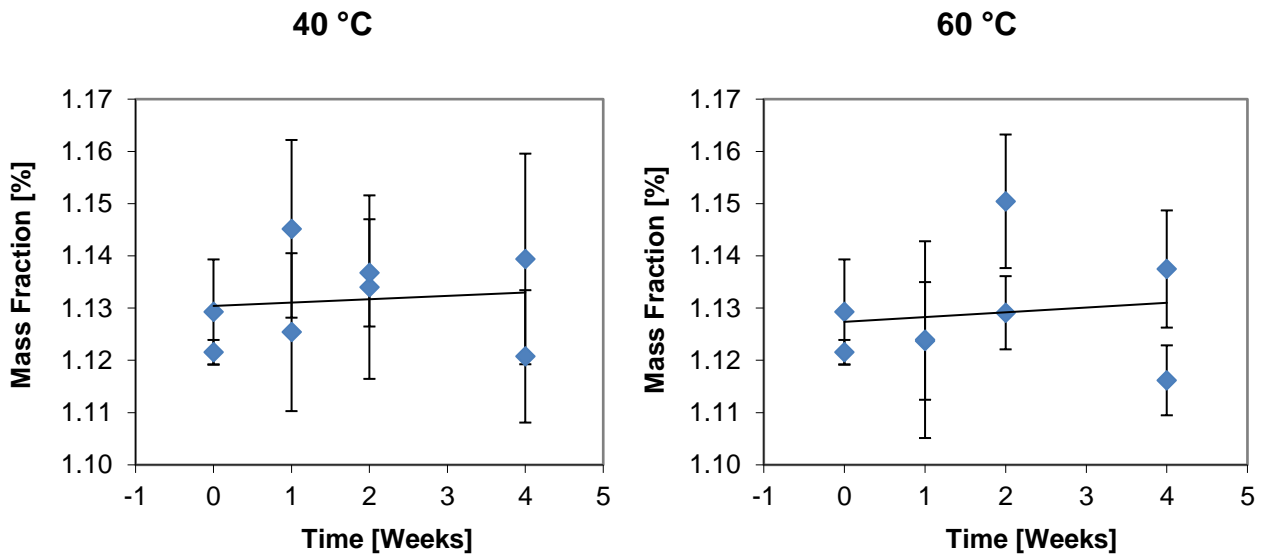
**Figure A2.3.** UME CRM 1205 short-term stability graphs for B



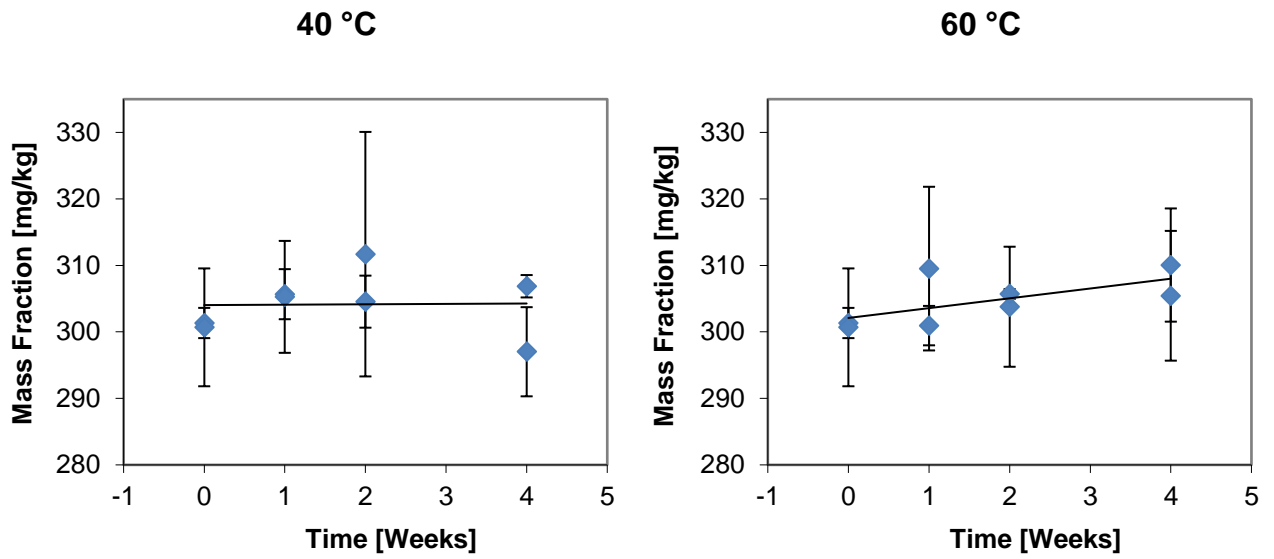
**Figure A2.4.** UME CRM 1205 short-term stability graphs for Ca



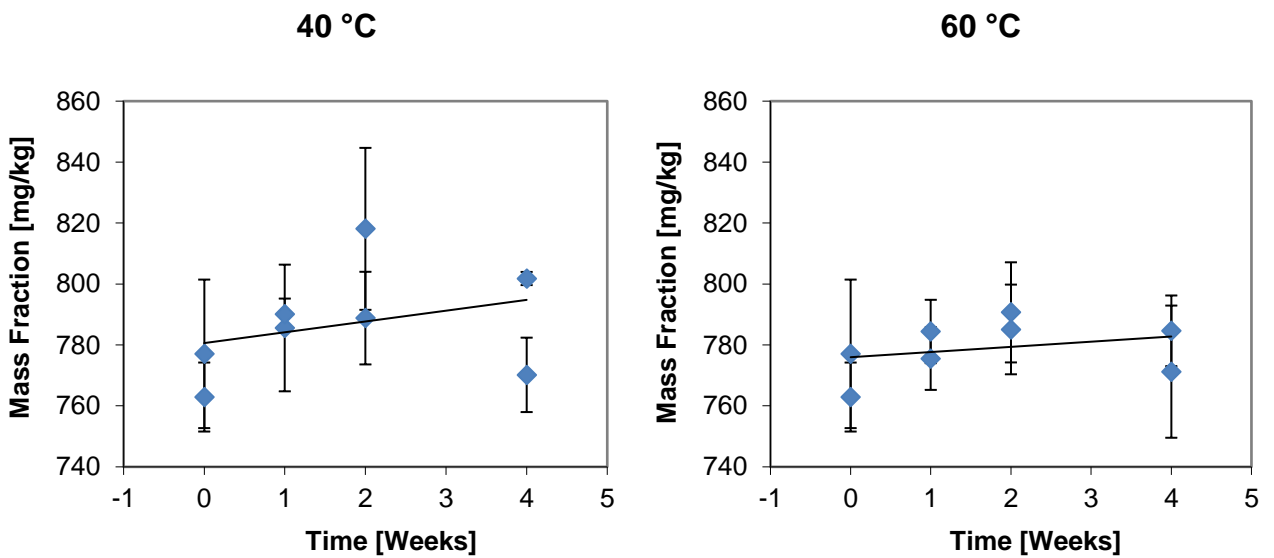
**Figure A2.5.** UME CRM 1205 short-term stability graphs for Fe



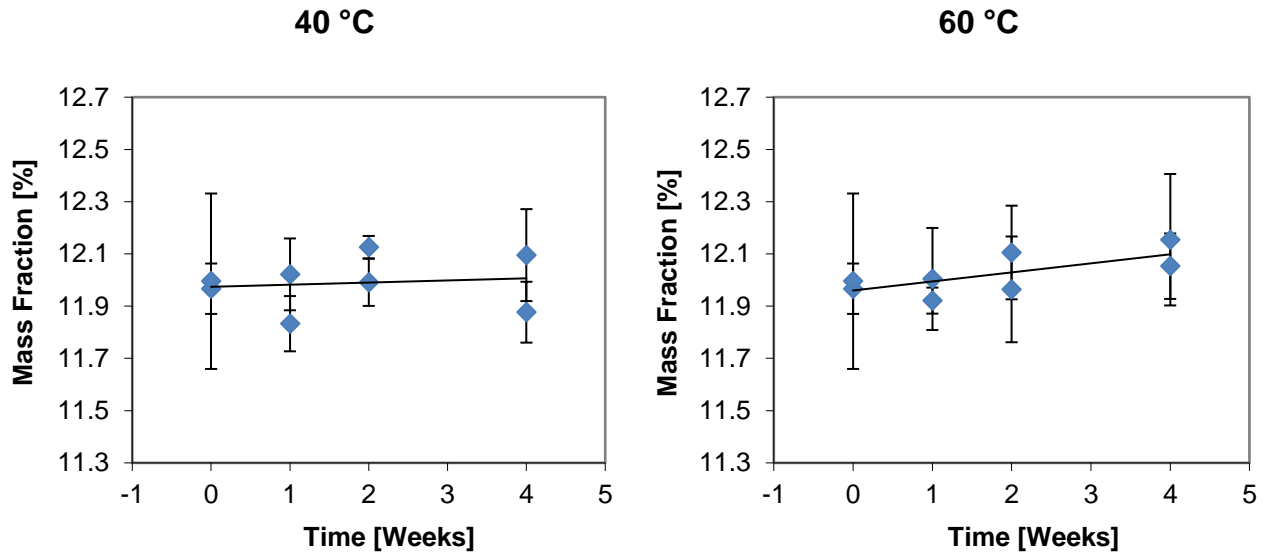
**Figure A2.6.** UME CRM 1205 short-term stability graphs for Mg



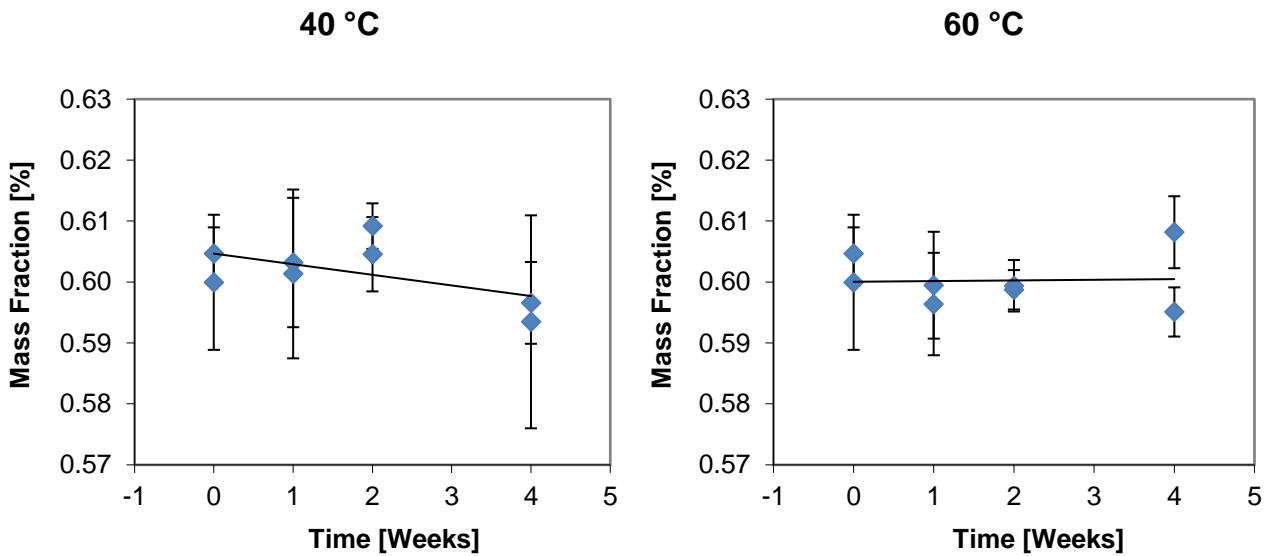
**Figure A2.7.** UME CRM 1205 short-term stability graphs for Na



**Figure A2.8.** UME CRM 1205 short-term stability graphs for S

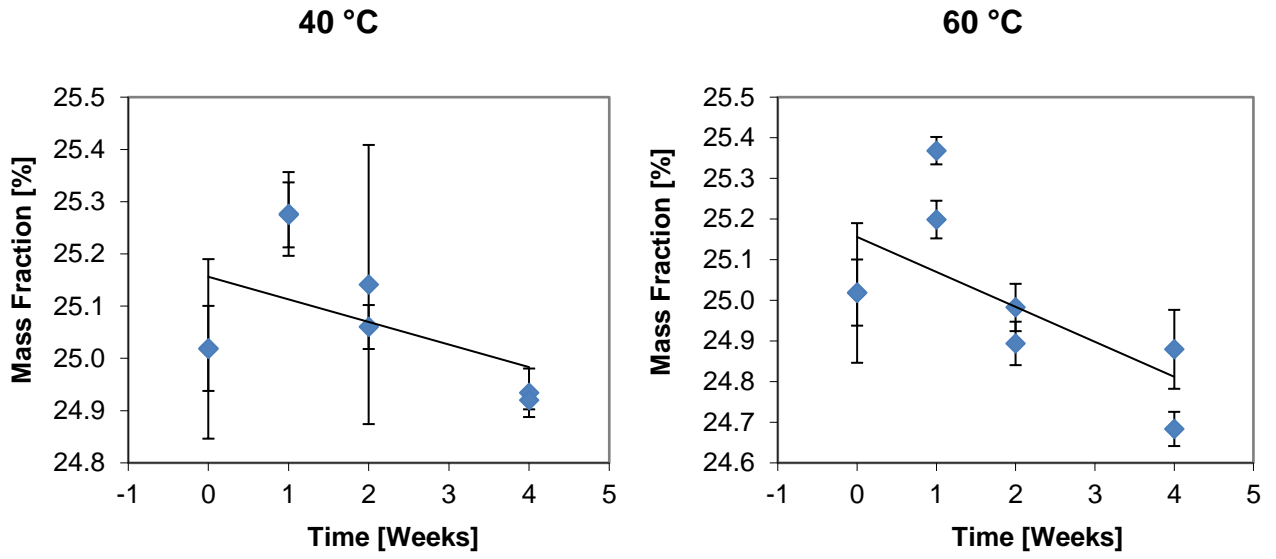


**Figure A2.9.** UME CRM 1205 short-term stability graphs for Si



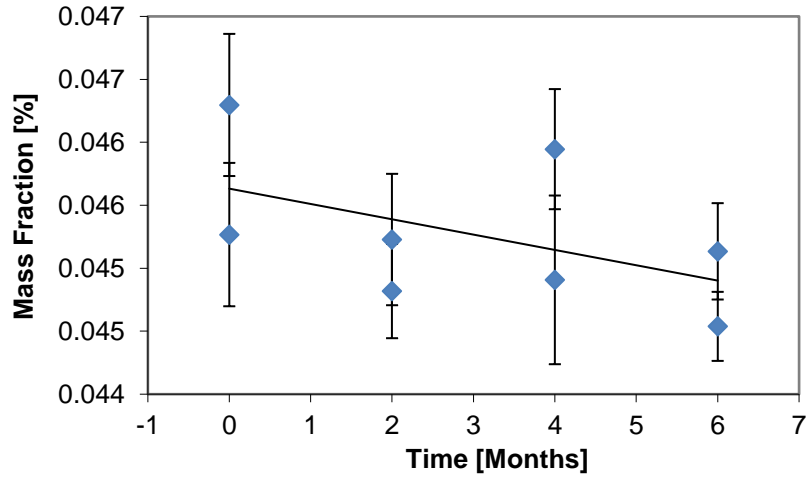
**Figure A2.10.** UME CRM 1205 short-term stability graphs for Sr



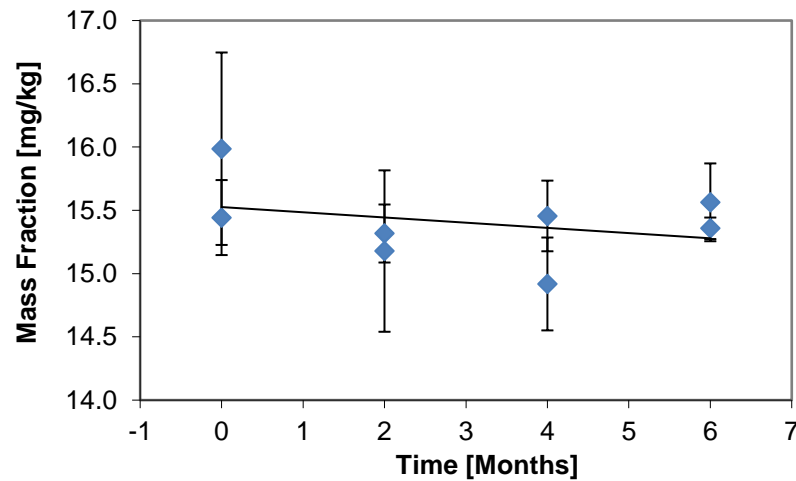


**Figure A2.11.** UME CRM 1205 short-term stability graphs for LOI

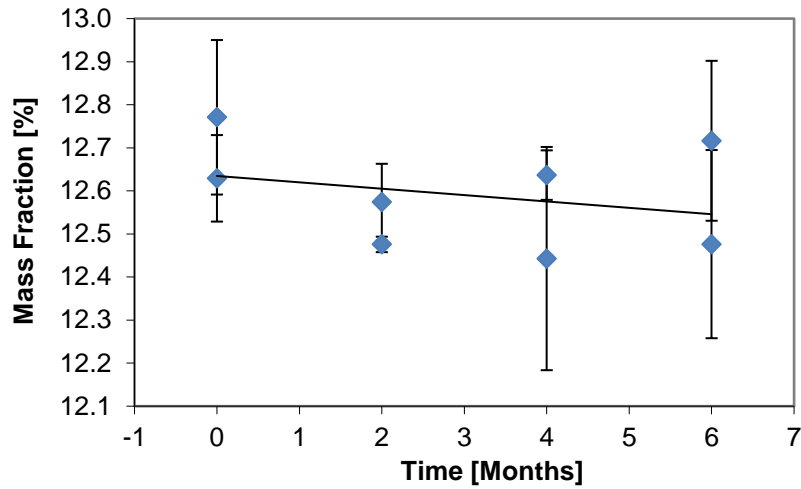
### Annex 3. Graphs for Long-Term Stability



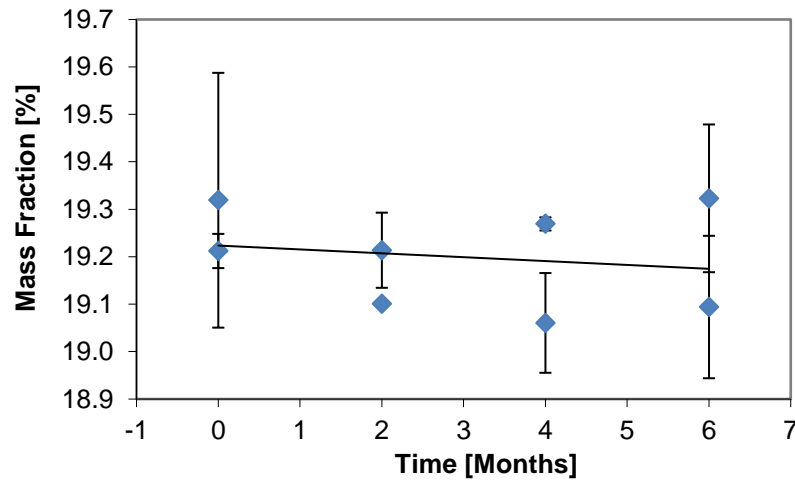
**Figure A3.1.** UME CRM 1205 long-term stability graph for Al



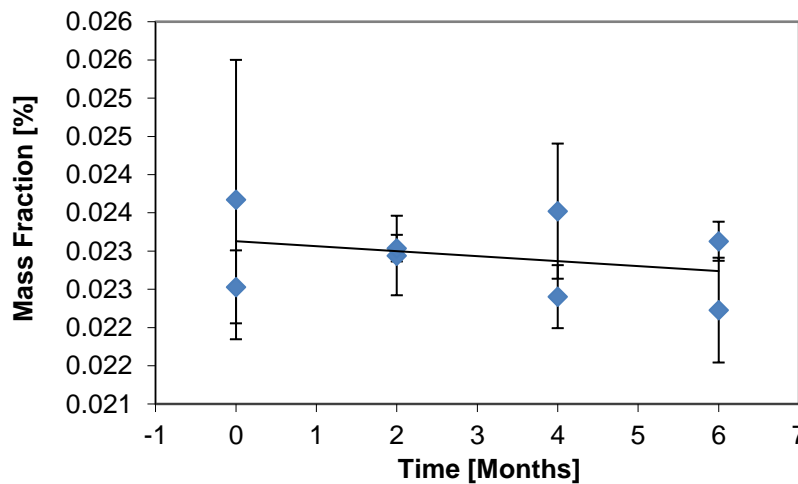
**Figure A3.2.** UME CRM 1205 long-term stability graph for As



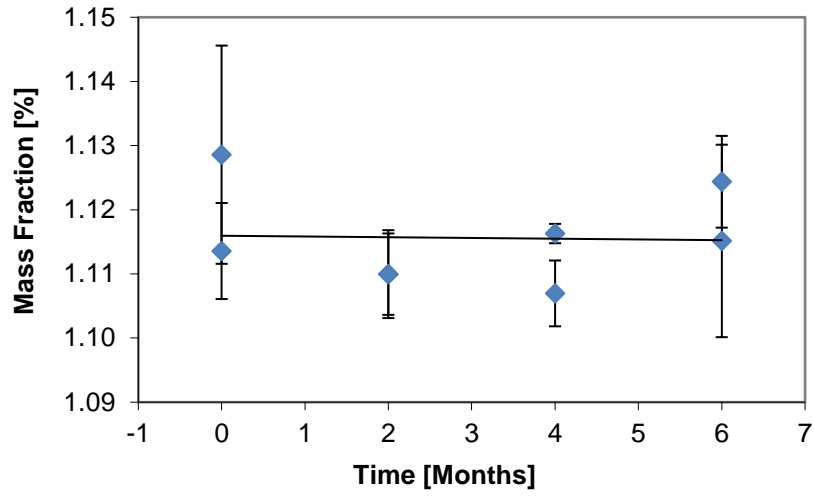
**Figure A3.3.** UME CRM 1205 long-term stability graph for B



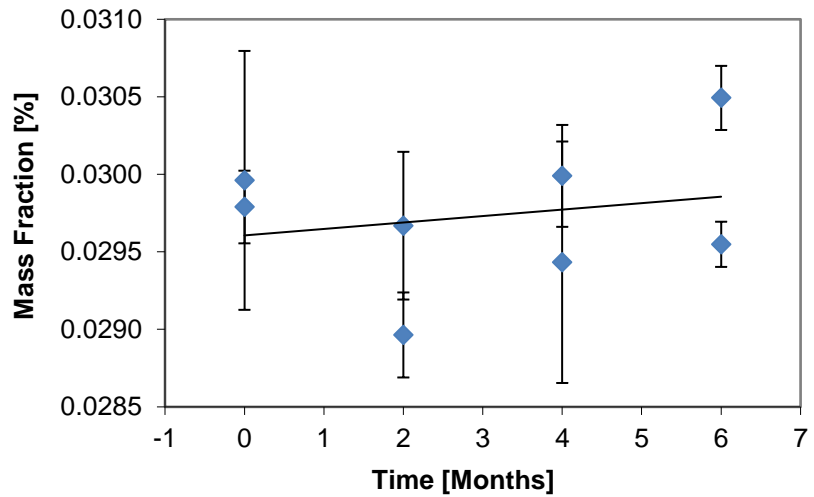
**Figure A3.4.** UME CRM 1205 long-term stability graph for Ca



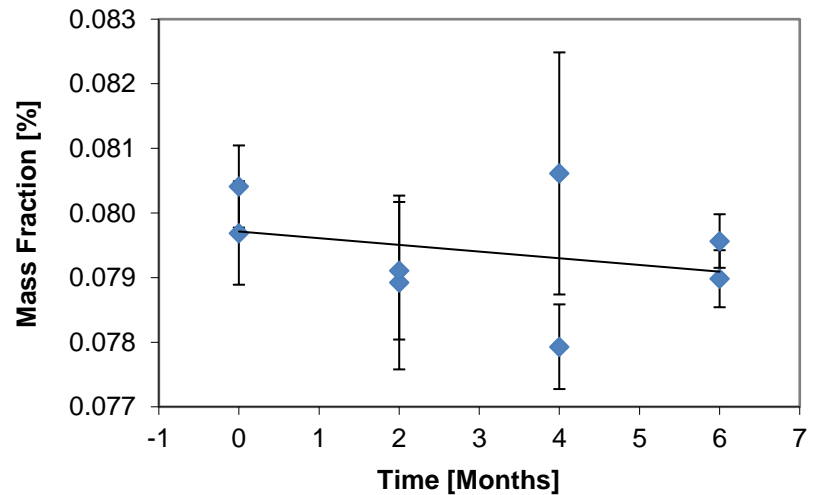
**Figure A3.5.** UME CRM 1205 long-term stability graph for Fe



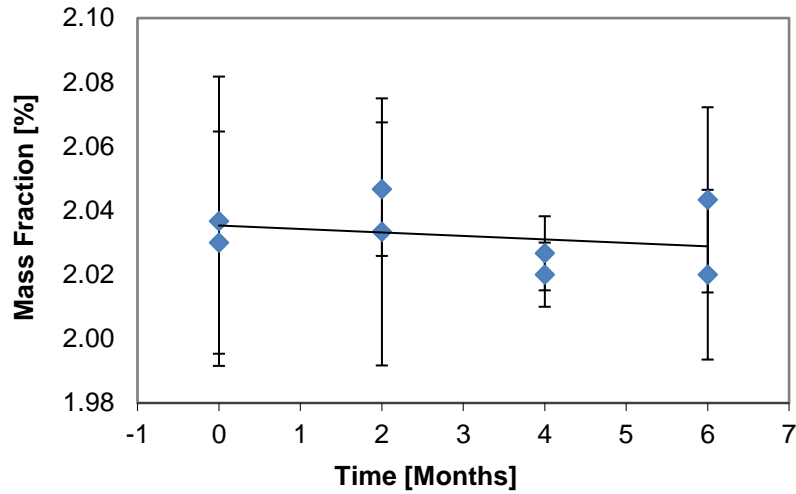
**Figure A3.6.** UME CRM 1205 long-term stability graph for Mg



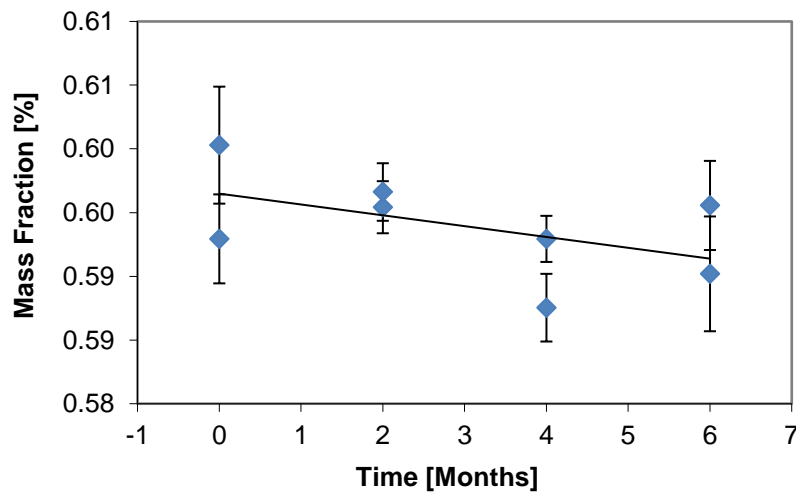
**Figure A3.7.** UME CRM 1205 long-term stability graph for Na



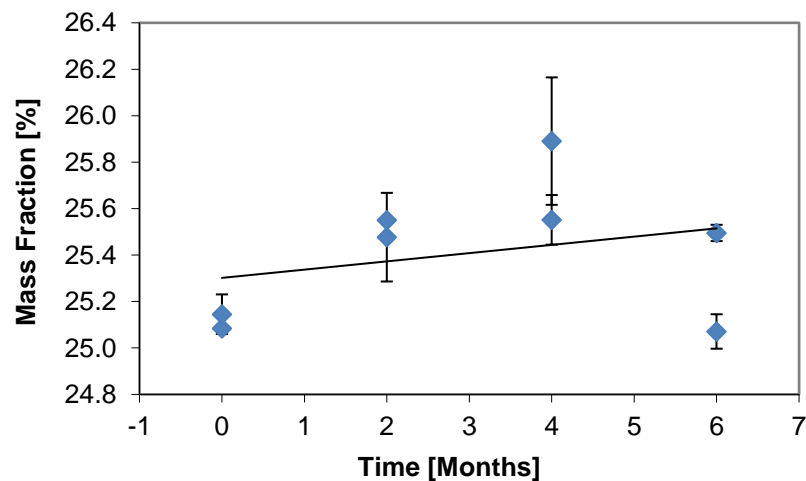
**Figure A3.8.** UME CRM 1205 long-term stability graph for S



**Figure A3.9.** UME CRM 1205 long-term stability graph for Si



**Figure A3.10.** UME CRM 1205 long-term stability graph for Sr



**Figure A3.11.** UME CRM 1205 long-term stability graph for LOI