PROFICIENCY TEST ROUND OF THE DETERMINATION OF TITANIUM (Ti) IN WASTE WATER

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Abstract

In 2017 the second round of proficiency testing of the determination of titanium in waste water was organized by Quality Control Department and Department of Environmental Protection of Cinkarna Celje. All procedures were done in accordance with ISO/IEC 17043 [1]. Based on experience by preparing and conducting the first round of titanium in waste water (2014), when only two laboratories participated, we decided to invite ten laboratories from Slovenia from different branches of industry, environment protection and university.

Nine laboratories were registered for MP-Ti 2017, eight laboratories reported results on time. Among them one laboratory was accredited (ISO/IEC 17025) for the determination of Ti in waste water; six laboratories were accredited for the determination of other elements in waste water.

Sampling of waste water at the standard sampling site located in the field of Titanium dioxide production and sample preparation were done by the Department of Environmental Protection of Cinkarna Celje. Preliminary assessment of titanium in waste water, homogeneity and stability evaluation were conducted. The sufficient homogeneity and stability were confirmed.

Each participant received a set of two samples: one for the determination of total titanium and other for the determination of dissolved titanium. One participant ordered three set of samples due to testing different methods for sample preparation. The sample preparation and the method for the determination of titanium were chosen by each participant. The participants reported two results for the determination of titanium for each sample. Together with results the sample preparation and the determination methods were reported.

Statistical assessment of the results was done according to ISO 13528 [5]. For small number of participants the robust statistical methods were used to evaluate assigned value and standard uncertainty for the assigned value. The performance assessment for participants was established by z-score.

The results of proficiency testing are discussed and presented in the final report.

Key words: **proficiency test round, determination of titanium in waste water.**

PURPOSE AND SCOPE OF PROFICIENCY TEST ROUND

Proficiency test round was planned and conducted for the purpose to evaluate the competence of participating laboratories for determination of titanium (Ti) content in waste waters.

The aim of the proficiency test round was:

- **to assess and improve the quality of procedures of sample preparation and verify different analytical methods of Ti determination in waste waters,**
- **to show confidence in our measurements to our customers and to the accreditation body, as no commercial interlaboratory comparison is available in the hereby proposed area.**

ORGANISATION

Proficiency test round has been organized by

- the **Department of Environmental Protection of Cinkarna Celje, INC.** – sampling and preparation of samples of waste water.
- the **Quality Control Department of Cinkarna Celje, INC.** – preparation of PT protocol, preliminary evaluation of Ti content in waste water (analysis), homogeneity and stability testing, sending samples to participating laboratories and preparation of final report with statistical analysis.

The **first proposal** for proficiency test round was sent to the laboratories in March 2017. **Nine** laboratories signed in to participate MP-Ti until April 3rd 2017, one of them requested for three complets of samples due to verify three different sample preparations. To ensure confidentiality, each laboratory has been assigned to a blind ID code from 1 to 11. All participants received complet of two samples with signs **MP Ti - ID (UNFILTERED SAMPLE and FILTRED SAMPLE)** on April 20th 2017 by mail and all of them sent the results in the prescribed form by June 1st 2017, except the participant with ID MP Ti – 07 (the analysis could not be perpormed because of the instrument failure) and the participant with ID MP Ti - 11, which sent the result for the unfiltered sample only.

The participants reported the **procedure of sample preparation** and **analytical methods** which were used for determination together with results of measurements.

HOMOGENEITY TESTING

The homogeneity study was conducted on **six sample units** - bottles (P) selected at random from all the test material prepared for distribution. Three subsamples (V) were taken from each bottle and three measurements (M) were performed on each of the selected subsamples for analysis in a random order by using a method of appropriate precision under repeatability conditions.

Table 1: The sufficient homogeneity [6] for both test samples was confirmed

Measurand	Cochran's test for outliers α = 0,01	Sufficient homogeneity ANOVA α = 0,01
Ti [mg/L] (Unfiltered sample)	$C < C_\alpha$	$F < F_\alpha$, $s^2_{sam} < C_{sh}$ **confirmed**
Ti [mg/L] (Filtered sample)	$C < C_\alpha$	$F < F_\alpha$, $s^2_{sam} < C_{sh}$ **confirmed**

STABILITY TESTING

For the stability test [6] the sample of waste water (one distribution unit - bottle) was randomly divided into four equal subsamples. One of them which is called control subsample was kept in laboratory refrigerator under condition of maximum stability (3°C ± 2°C), the other three were treated as experimental subsamples; first of them was exposed to outside weather conditions (10°C - 23°C), the second was kept in storage facility (21°C ± 3°C) and the third one was put in the handy refrigerator (6°C ± 3°C). Measurements were scheduled from April 2017 to June 2017 for two weeks period. The samples were analysed simultaneously in random order under repeatability conditions according to the schedule.

Table 2: The stability for both test samples for the period of proficiency test round was confirmed

Measurand	Difference between control and experimental subsamples ANOVA (α = 0,05)	Time dependent stability – trend analysis – slope does not differ significantly from zero	Overall stability – difference between average measurements in the homogeneity and stability study
Ti [mg/L] (Unfiltered sample)	$F < F_\alpha$	$\lvert \bar{X}_h - \bar{X}_s \rvert \leq 0{,}3\sigma_p$	$\lvert \bar{X}_h - \bar{X}_s \rvert \leq 0{,}3\sigma_p$
Ti [mg/L] (Filtered sample)	$F < F_\alpha$	$\lvert \bar{X}_h - \bar{X}_s \rvert \leq 0{,}3\sigma_p$	$\lvert \bar{X}_h - \bar{X}_s \rvert \leq 0{,}3\sigma_p$

PERFORMANCE ASSESSMENT

Establishing the assigned value (X_a) and standard uncertainty on the assigned value ($u(X_a)$)

Table 3: Estimation of the assigned value as the **consensus** of participants' results [5, 7]

Determination in **unfiltered sample** of waste water	Average	Standard deviation	Robust average	Robust standard deviation	**Assigned value**	Uncertainty on the assigned value
	$\bar{X}$	s	X_{rob}	s_{rob}	X_a	$u(X_a)$
Ti [mg/L]	0,198	0,0292	0,193	0,0206	**0,193**	**0,0082**

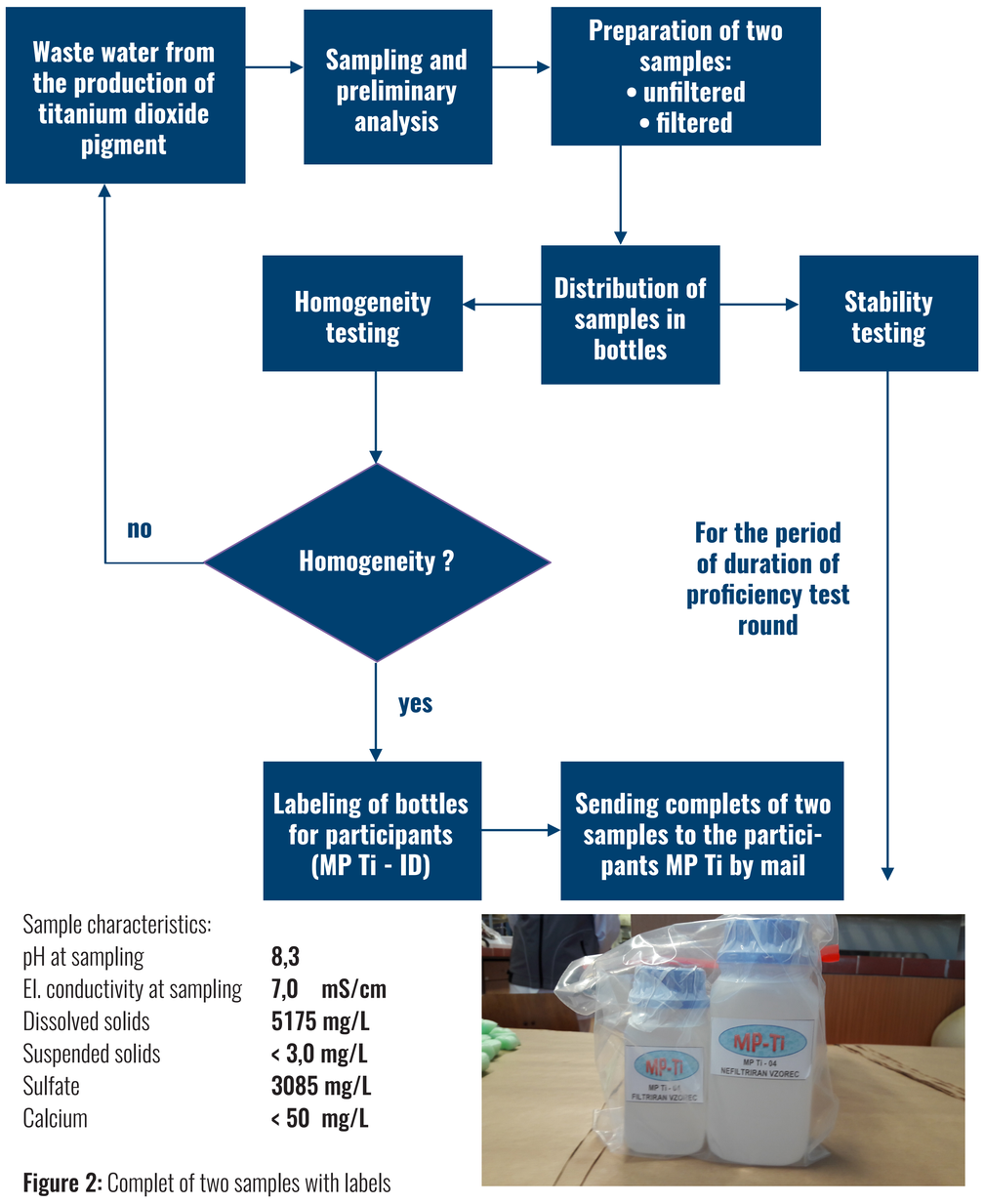
Table 4: Estimation of the assigned value as **CRM addition** on the matrix of waste water for filtered sample [5].

Determination in **filtered sample** of waste water	Average difference between CRM and participants' resulst	Uncertainty of the difference	Value of CRM addition	Uncertainty of CRM addition	**Assigned value**	Uncertainty on the assigned value
	$\bar{d}$	$u_{\bar{d}}$	X_{CRM}	u_{CRM}	X_a	$u(X_a)$
Ti [mg/L]	0,0005	0,0029	0,1003	0,0008	**0,1008**	**0,0030**

SAMPLING AND SAMPLE PREPARATION

Figure 1: Sampling location and procedure [3, 4]
Preparation of **unfiltered** sample:
Conservation of sample: addition of nitric(VI) acid to pH < 2.

Preparation of **filtered** sample: Filtration through 0,45 µm filter.
Conservation of sample: addition of nitric(VI) acid to pH < 2.



Sample characteristics:

pH at sampling	**8,3**
El. conductivity at sampling	**7,0 mS/cm**
Dissolved solids	**5175 mg/L**
Suspended solids	**< 3,0 mg/L**
Sulfate	**3085 mg/L**
Calcium	**< 50 mg/L**

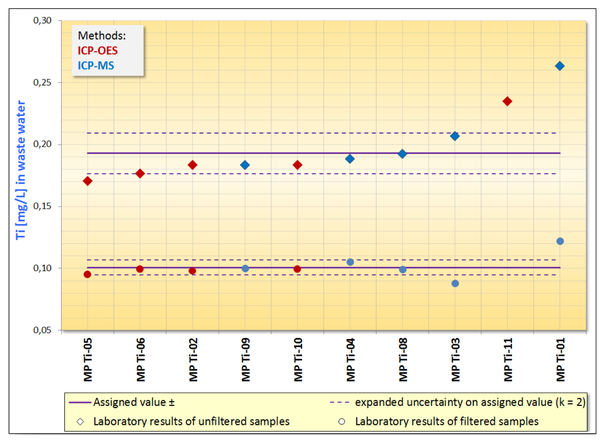
Figure 2: Complet of two samples with labels

RESULTS

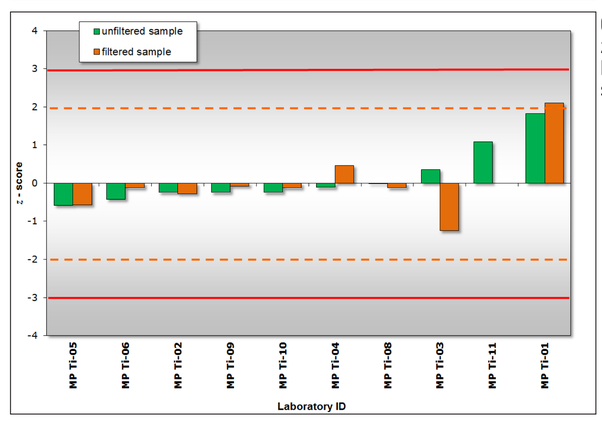
Table 5: Results of measurement and z-scores for individual laboratories [2, 5]

Participient's identification code (ID)	Results: Unfiltred sample [mg/L]	Results: Filtred sample [mg/L]	Unfiltered sample preparation	Method	z - score: Unfiltred sample	z - score: Filtred sample
MP Ti - 01	0,264	0,122	MW* HNO_3/HF	ISO 17294-2 modif. **ICP-MS**	**1,83**	**2,10**
MP Ti - 02	0,184	0,098	OD** H_2SO_4/ $(NH_4)_2SO_4$	ISO 11885:2007, **ICP-OES**	**-0,25**	**-0,28**
MP Ti - 03	0,207	0,0882	MW* HNO_3/ HCl/HF	ISO 17294-2:2005 **ICP-MS**	**0,36**	**-1,25**
MP Ti - 04	0,189	0,1055	OD** H_2SO_4/ $(NH_4)_2SO_4$	**ICP-MS**	**-0,12**	**0,47**
MP Ti - 05	0,171	0,095	OD** HNO_3	ISO 11885:2007 **ICP-OES**	**-0,58**	**-0,57**
MP Ti - 06	0,177	0,0995	SIST EN ISO 15587-2:2003 modif.	ISO 11885:2007 **ICP-OES**	**-0,43**	**-0,13**
MP Ti - 08	0,193	0,0995	SIST EN ISO 15587-2:2003 modif.	ISO 17294-2:2005 **ICP-MS**	**-0,01**	**-0,13**
MP Ti - 09	0,184	0,100	Wet incineration HCl	Internal **ICP-MS**	**-0,25**	**-0,07**
MP Ti - 10	0,184	0,0995	HNO_3	ISO 11885:20097 **ICP-OES**	**-0,25**	**-0,13**
MP Ti - 11	0,235	-	MW* HNO_3/HF	ISO 11885:2007 **ICP-OES**	**1,09**	-

*MW – microwave digestion
**OD – open digestion



Graph 1: Laboratory results for Ti content measurement in unfiltered and filtered samples with regions of assigned value ± its expandad uncertainties (k = 2):



Graph 2: Bar chart of z-scores of individual laboratory for both samples.

CONCLUSIONS

Eight laboratories from different organisations (industry, scientific institutes and university, national institutes) participated in proficiency test round. For the determination of Ti content in waste water two different instrumental techniques were used: ***ICP-OES*** (Inductively Coupled Plasma – Optical Emission Spectrometry) and ***ICP-MS*** (Inductively Coupled Plasma – Mass Spectrometry). ***Four different combinations of reagents*** were carried out for digestion of unfiltered samples. All the participants reached ***z-scores < 2,5 for unfiltered and filtered samples.*** The differences of results between two different instrumental techniques were not significant, but we noticed the influence of preparation (digestion) of unfiltered samples on the result of measurement.

REFERENCES

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