

Total Solid (TS) and Total Volatile Solid (TVS) at VERITAS with Thermogravimetry in Wastewater and Sewage Sludge

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Introduction

One of the most important ways to keep our environment clean and preserve nature for future generations is through water treatment. For this process to be successful, laboratory-based quality control is crucial. This paper describes an example of total solids (TS) and total volatile solids (TVS) determination at an important water treatment facility in Italy.

VERITAS S.p.A (Veneziana Energia Risorse Idriche Territorio Ambiente e Servizi) is the largest multi-utility water treatment facility in Veneto and one of the largest in all of Italy performing both waste collection and treatment and an integrated water cycle.

VERITAS S.p.A has about 3,000 employees and a turnover of approximately € 369 million (2020 data). Within the company, there is an analysis laboratory, accredited under ISO IEC 17025:2018, which performs the biological and chemical analyses required to maintain drinking water quality and improve environmental impact. VERITAS activities and infrastructure for the integrated water service can be summarized as follows (Data updated to 12/31/2020):

- Drinking water distributed: 78 million cubic meters
- Water invoiced from the industrial aqueduct: 5.7 million cubic meters
- Purified wastewater: 88 million cubic meters
- Water network: 5,343 km (5,714 km with the adduction network)
- Sewerage: 2,768 km
- Purification plants: 37
- Drinking and disinfection plants: 14
- Tanks: 85
- Withdrawal points (aquifers and surface sources): 73

Sludge is a fundamental part of the water treatment process and the main residue of the purification treatments.

Most water purification processes usually involve the production of sludge, consisting of concentrated suspensions of the materials removed during the various treatments; therefore, knowing the various characteristics of the sludge (specifically TS and TVS) in real time is essential for the efficient management of the process.

The moisture, ash, and volatile matter of the sludge samples are some of the main parameters used to calculate key process control metrics such as sludge load and age.

In addition to those main parameters, there are numerous other definitions found in Table 3 for a fuller characterization of the sludge.

- **"Total Solids" (TS)** is the residue that remains in a crucible after the evaporation of a sludge sample and its subsequent drying in an oven at a temperature of 105 °C, otherwise defined as Residue at 105 °C, Dry Residue (DR), or Mixed Liquor Suspended Solids (MLSS). Moisture, or water content, is its inverse.
- **"Total Fixed Solids" (TFS)** are determined after incineration at 550 °C, otherwise defined as Ash.
- **"Total Volatile Solids" (TVS)** or Mixed Liquor Volatile Suspended Solids (MLVSS), are obtained by finding the difference between the value of the TS and that of the TFS. They constitute an evaluation index of the content of the organic substances in the sludge.

VERITAS' laboratory assumes that dissolved solids are negligible relative to the MLSS for non-saline matrices. This has been checked by specific studies in consideration of the plants' needs and to overcome the operational limits of the large number of filtrations otherwise required to remove dissolved solids.

This assumption derives from the need to speed up and optimize the process, thus making time-sensitive information about the composition and characteristics of the sludge rapidly available to the operators of the plants.

In fact, the experimental evidence has shown that there are no statistically significant differences between the results of TS and MLSS.

In addition, automation of the method has led to an improvement from an analytical point of view, allowing the daily analysis of a large number of samples and the sequential determination of TS and TVS. The precision is improved, handling errors are reduced, and the whole process is controlled in a more accurate way by the instruments' software. Verification of the results is done using a certified reference material (CRM).

The VERITAS S.p.A laboratory has 4 LECO TGA instruments (3x LECO TGA701 and 1x LECO TGA801). The LECO TGA systems can analyze up to 19 (38) samples simultaneously. The samples, whether solid, slurry, or liquid, are put in ceramic crucibles. Up to 19 crucibles are placed in a carousel that moves the crucibles to an integrated balance so that every sample gets a mass reading every few minutes. A step program can be entered: the method used at VERITAS keeps the temperature at 105 °C for all samples to determine moisture/TS, and then raises the temperature to 550 °C to determine the ash/TFS content. The system is capable of temperatures up to 1000 °C, and different atmospheres can be used (e.g. air, oxygen, nitrogen).

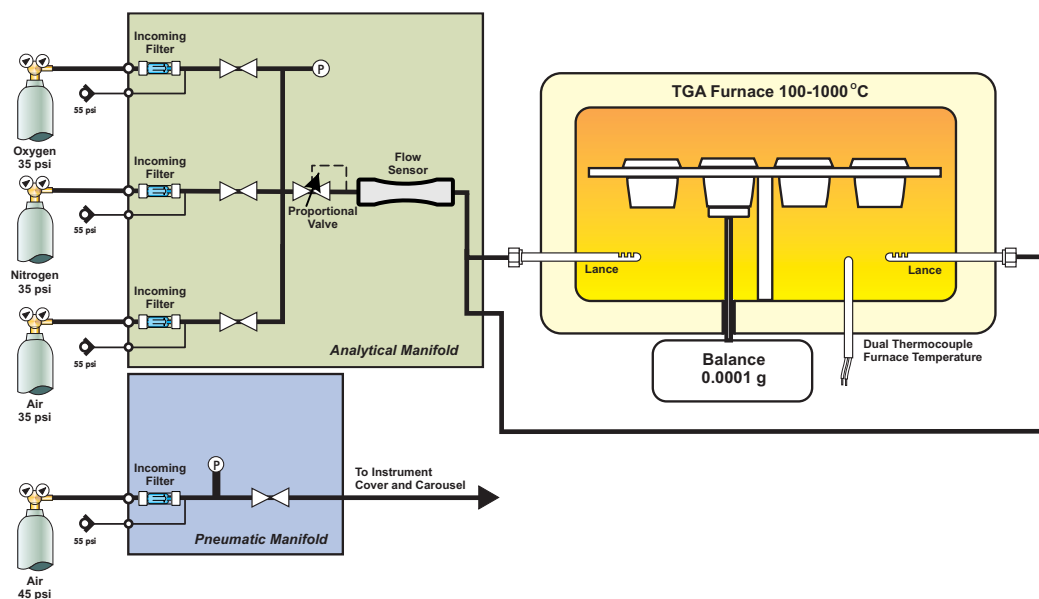


Figure 1: General schematics of LECO TGA801



Figure 2: TGA801 open with crucibles – Picture of crucible carousel

Table 1: Examples of Sludge/Wastewater

Sample Name	Total Solids TS	Total Fixed Solids
Sludge	18.53 %	5.801 %
Sludge	18.51 %	5.813 %
Sludge	18.55 %	5.822 %

Sample Name	Total Solids TS	Total Fixed Solids
Water A	0.15 %	0.072 %
Water A	0.15 %	0.068 %
Water A	0.18 %	0.086 %

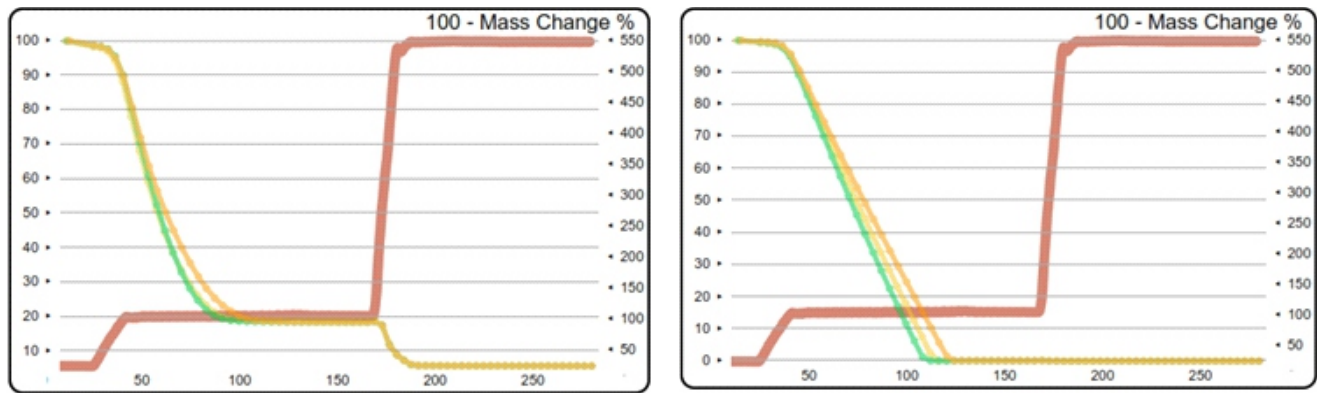


Figure 3: Typical results for sludge and wastewater are shown in Table 2

Table 2: Soil sample as a test sample

Sample ID	Total Solids (TS) in %	Total Fixed Solids (TFS) in %	Total Volatile Solids (TVS) in %
39177 - soil	91.38	2.01	89.37
39177 - soil	89.79	2.06	87.73
39177 - soil	90.18	2.11	88.07
39177 - soil	89.77	2.02	87.75
39177 - soil	89.21	2.04	87.17
39177 - soil	89.27	2.05	87.22
39177 - soil	89.51	2.05	87.46
39177 - soil	89.09	2.13	86.96
39177 - soil	90.08	1.98	88.10
39177 - soil	89.05	2.10	86.95
	Avg = 89.73	2.06	87.68
	s = 0.70	0.05	0.73

Table 2 shows a test on 10 replicates of a soil sample as an example of method precision for the determination of TS, TFS, and TVS.

Table 3: Example of a report customized according to the needs of VERITAS Laboratory

Sample ID	TS %	TVS %	FTS %	Sol Tot Vol %	Vol. Sludge (L)	Mat. Sed. 30' (mL/L)	SSV (g/L)	SVI (mL/g)	MLVSS DR in %	TFS (mg/L)	TVS (mg/L)	ST DR-MLSS (mg/L)
45858	0.97	0.72	0.25	74.46	0.0191	300	2.70	82.61	74.46	927.4	2704	3632
45863	1.47	1.04	0.43	71.00	0.0191	490	3.57	97.58	71.00	1456	3565	5021
45218	1.36	0.84	0.52	61.88	0.0191	900	3.43	162.4	61.88	2113	3430	5543
45219	1.20	0.74	0.46	61.45	0.0191	840	3.02	171.1	61.45	1893	3017	4911
45923	0.91	0.64	0.27	70.20	0.0191	400	2.26	124.2	70.20	959.8	2261	3221

Sample ID: Sample ID

TS %: Total Solids (105 °C)

TVS %: Total Volatile Solids on the mass of liquid sludge

TFS %: Total Fixed Solids on the mass of liquid sludge (550 °C)

Sol Tot Vol %: Total Volatile Solids on the total of Total Solids (DR)

Vol. Sludge (L): Sludge volume used for the test

Mat. Sed. 30' (mL/L): Material after 30' of sedimentation

SSV (g/L): Total volatile solid on the liquid sample

SVI (mL/g): Sludge volume index

MLVSS DR in %: Total volatile solid on total solid

TFS (mg/L): Total fixed solid on the liquid sample volume

TVS (mg/L): Total volatile solid on the liquid sample volume

ST DR-MLSS (mg/L): total solid on the liquid sample volume

The reference method chosen by VERITAS laboratory for the determination of TS is: CNR IRSA 2 Q 64 Vol 2 1984 / Newsletter of the analytical methods CNR IRSA n.2: 2008.

All tests conducted through the thermogravimetric analyzer are therefore subject to the operational parameters and nomenclature of this method. The adoption of an automated method to the given normative regulations has been checked. The parameters described in the method can be used with the same calculations without any substantial modifications.

The accreditation of a test method by Accredia (Accredia – L'Ente Italiano di Accreditamento - Italian accreditation authority) indicates that the third party guarantees that the test is performed in accordance with the relevant normative legislation. The determination of the TS, TVS, and TFS is one of the determinations that the VERITAS laboratory decided to follow via a QC control process under ISO certification a long time ago; therefore, it follows that the entire operational process, equipment, analytical results, and the technicians themselves, are subjected to periodical audits to keep the entire process under control.

Both the oven/temperature and the balance of the TGA determinators are subject to specific and detailed calibration verification procedures. In addition, the use of certified reference materials and specific control charts allow for verifying the repeatability and accuracy of the method.

Conclusion

The number of samples processed and the importance of the results at VERITAS required the introduction of automatic thermogravimetric analyzers instead of the classic operating methods. The automated approach allows the VERITAS laboratory to process about 6,000 liquid and solid sludge samples annually maintaining and guaranteeing a very high-quality standard, demonstrated by the accreditation of the test with the Italian National Accreditation Entity ACCREDIA, who is appointed by the Italian government to attest the competence, independence, and impartiality of Conformity Assessment Bodies (CABs) which verify the conformity to the standards of goods and services.