

Uncertainty measurement in Mobile optical Emission spectrometer

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Abstract

Chemical properties of the raw materials, used during fabrication of various components for industries are identified normally from manufacturer's test certificates. When a separate representative sample of the component is not available, identification of materials are made directly on the component using portable X-Ray Fluorescence (XRF) or mobile OES. In order to compare the results of Mobile OES vs Lab OES, Uncertainty in measurements between Lab version and mobile version OES was done for major and minor elements of the SS material samples. A CRM sample conforming to SS304L and SS316L along with one set of SS samples from various projects were selected and the chemical composition of each samples was tested using mobile version OES. The same samples were tested at three different NABL accredited labs at Chennai using Lab version. The expanded uncertainty for each method was calculated using standard NABL 141 and results was plotted. It was observed that Uncertainty of the Mobile OES results are very closer to the Lab version for all elements except a slight variation in Cr and Ni by 0.1% in terms of uncertainty. When comparing the actual compositions, the amount of percent composition of the Cr and Ni element is lesser than the lab version values and the variation is within the permitted tolerance values. The study had given valid information for improving confidence and helps to standardize the test procedures for material identification.

Introduction :

Chemical properties of the raw materials such as castings, forgings, wrought products, plates, pipes, rounds, etc. used during fabrication of various components or the fabricated products of petrochemical, automobile, defense, nuclear industries are identified normally from manufacturer's test certificates. When the material procurement quantity of particular product & grade is small, continuity in the material identification history get missed in some practical situations during various manufacturing/ fabrication processes. Under such conditions, Positive Metal Identification(PMI), is the only available option to establish the traceability of chemical composition. In this method chemical analysis will be conducted non-destructively on the finished product. There are two methods generally used for Positive metal identification, Mobile Optical emission spectroscopy(OES) and X-ray fluorescent spectroscopy(XRF).

XRF Spectroscopy:

In XRF spectrometry ,High energy primary X-ray Photons are emitted from a X-ray source and strike the sample .The primary photons from X-ray source have enough energy to knock electrons out of the innermost orbit, and atoms becomes unstable and try to fill the vacancy during this phenomena electron moves from the outer orbit to inner cell, in this process it emits energy that is known as secondary X-ray. The secondary X-ray produced is characteristics of a specific element . The Number of element specific characteristics X-rays produced in a sample over a given period of time or intensity measured. This determines the quantity of the given element in that sample.

Advantage: Analysis is very fast, very handy, non destructive, skilled operator not required.

Disadvantage : It can not detect carbon, poor detestability for other light elements like P, S, Si etc.

Optical Emission Spectroscopy

As we have seen the major disadvantage of XRF is it can not detect carbon we know that carbon plays a key role in steel industry, hence steel industry depends on OES method of chemical analysis. Optical emission spectrometry involves applying electrical energy in the form of spark generated between an electrode and a metal sample, whereby the vaporized atoms are brought to a high energy state within a so-called "discharge plasma". These excited atoms and ions in the discharge plasma create a unique emission spectrum specific to each element, as shown at right. Thus, a single element generates numerous characteristic emission spectral lines. Therefore, the light generated by the discharge can be said to be a collection of the spectral lines generated by the elements in the sample. This light is split by a diffraction grating to extract the emission spectrum for the target elements. The intensity of each emission spectrum depends on the concentration of the element in the sample. Detectors (photomultiplier tubes/CCD) measure the presence or absence of the spectrum extracted for each element and the intensity of the spectrum to perform qualitative and quantitative analysis of the elements. Now a days Advanced instruments are coming it can cover almost full spectral range required for optical emission spectrometer, i.e **160 to 800 nm** range, each element with best spectral lines for individual matrices can be selected.

Advantage: It can detect most of the elements required for steel precisely, fast and reliable analysis.

Disadvantage: It need skilled operator, surface preparation, UHP argon for better result.

Uncertainty and its importance:

Uncertainty : Uncertainty is defined as a parameter, associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand. Type A evaluation (of uncertainty) is Method of evaluation of uncertainty by the statistical analysis of series of observations and Type B evaluation (of uncertainty) is Method of evaluation of uncertainty by means other than the statistical analysis of series of observations.

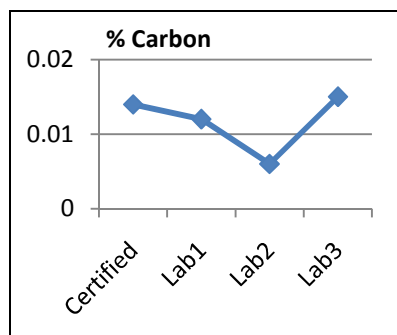
The true values of a measurand is an ideal concept, practically true value can not be measured, but it is very important how accurately or closely one quantity can be estimated of its true value. The quantity of uncertainty of measurement indicates its quality of measurement. Measurement along with its uncertainty is also required to evaluate the capability of the method.

Experimental Details

In Nuclear plants and projects, major portion of structural materials selected are Austenitic Stainless steel type 304L and 316L to provide physical, chemical, mechanical, nuclear properties under high temperature and irradiation environments. A CRM sample conforming to SS304L and another with SS316L along with one no. of SS 304, SS316 samples representing reactor and reprocessing projects respectively were selected and chemical composition of each sample was tested using mobile version OES and XRF method at QAD, IGCAR, Kalpakkam and recorded the results. The same samples were sent to three different NABL accredited labs at Chennai for chemical analysis using Lab version OES and the results were recorded.

Inter lab Comparison:

Test results of CRM samples received from three different labs (A, B & C) were compared with the certified values of CRM samples and Lab A was found very close to certified values of certificate with respect to more number of alloying elements. The test value of Lab A has been selected to represent Lab version OES method for further comparison with mobile version. The line graph shows an example of the deviation of lab values of Carbon with respect to the corresponding certified values.

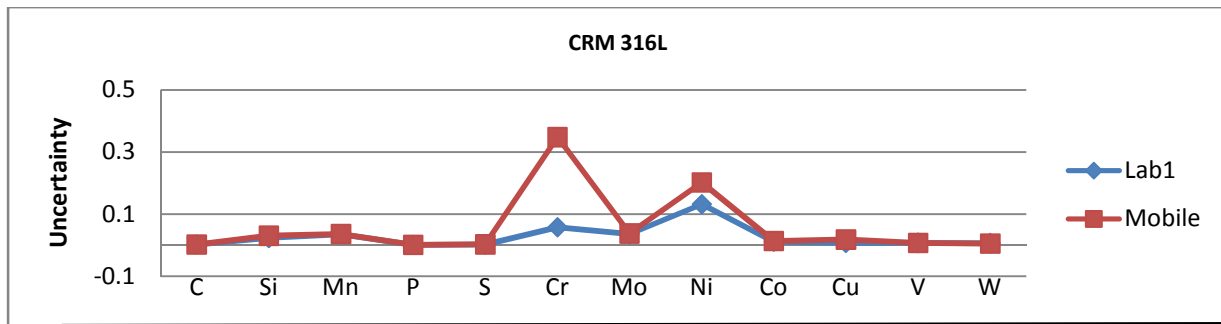
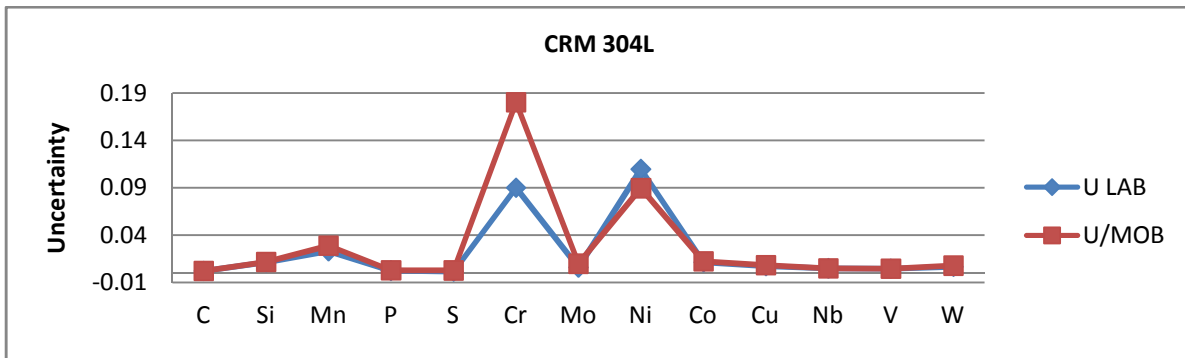


Measurement Uncertainty of Lab and Mobile OES methods: In general as per NABL standard 141, uncertainty is defined as a parameter, associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

For our Uncertainty calculation, three recorded test results from Lab A and Mobile OES was considered. Then uncertainty has been measured separately for Lab A and Mobile OES as per the procedure given in NABL 141. Expanded uncertainty was calculated separately for 304L CRM & 316L CRM sample for Lab and mobile version.

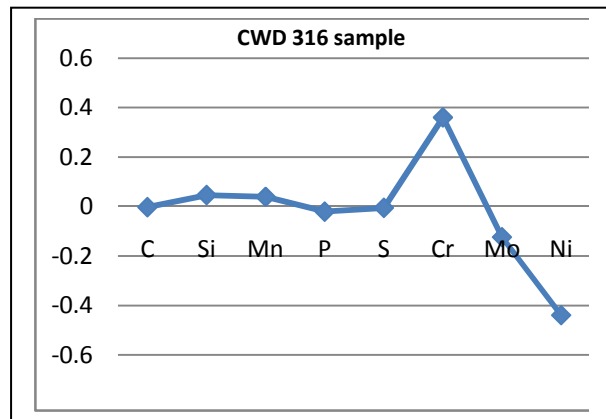
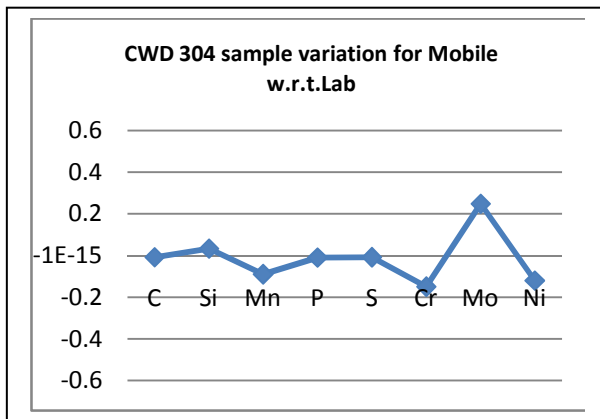
Comparison of Uncertainty of 304L and 316 L CRM samples:

The following graph shows the comparison of Uncertainties of 304L & 316L CRM sample measured Lab version results and mobile version results. Uncertainty values of 304L are deviated more in Chromium and Nickel elements when compared to all the other elements.



Variation of Mobile version OES w.r.t Lab version OES using SS304 & SS316 Project Samples:

After this uncertainty comparison for CRM samples, Product samples collected from various sites were tested with mobile and Lab version instruments and the variation in average values of the major elements for product samples for Lab and mobile OES were compared.



Discussion:

From the above experiments using CRM samples for Uncertainty comparison and project samples for variation w.r.t. lab values, the amount of percent composition of the particular element also contributes to difference. Because in case of Cr and Ni & Mo the tolerance range is larger compare to light element like C, S, & P. hence in some cases more deviation was observed for these elements.

Conclusion: From this experiment, it was observed that Uncertainty of the Mobile OES results are very closer to the Lab version for all elements except a slight variation in Cr and Ni by 0.1% in terms of uncertainty because the tolerance range of Cr and Ni is larger compare to light elements like C, S & P.

When comparing the actual compositions, the amount of percent composition of the Cr and Ni element is lesser than the lab version values and the variation is within the permitted tolerance values.

The study had given valid information for improving confidence and helps to standardize the test procedures.

