Session: New Developments / State of the Art Trace Profession

"Laser Ablation ICP-MS in Forensic Glass Analysis: A Decade of Experience"

Abstract

Based on (and referring to) the work of our group presented by Wilfried Stoecklein at the last Trace Evidence Symposium, further developments in the field of laser ablation ICP-MS in forensic glass analysis will be described. A focus is set on the quantitative analysis of glass fragments and the evaluation of match criteria for routine case work.

Introduction

Ten years ago at the last Trace Conference in San Antonio Dr. Wilfried Stoecklein presented his work titled "The Forensic Analysis of Float-Glass- Characterisation of Glasses from International Sources". The use of inductively coupled plasma-mass spectrometry (ICP-MS) for forensic glass case work was evaluated and described. Several aspects such as accuracy of results, comparability with other elemental analysis techniques such as XRF, source identification and differentiation of float glasses were covered by this work.

Based on this sound foundation our group introduced the technique of laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) to the field of quantitative analysis of float glasses. The results of our efforts will be described in this paper. Because it serves as a perfect starting point for our present work, Wilfried Stoecklein's conclusion of his work presented ten years ago is stated below: "In the forensic examination of glass, the comparison of flat glass plays a dominant role. Today it is manufactured by the float process in about 169 plants throughout the world. Refractive index measurements are not recommended for discriminating between float glass samples from various

manufacturers and plants. More than 10 % of the examined float glass from 32 plants is indistinguishable by applying discrimination tests. These results show that type II errors, i.e. incorrectly attributing two samples to a common source, are possible if the results of a glass comparison are only based on R.I. measurements. Greater reliability can only be placed in the correctness of a common source conclusion if a method for elemental analysis is available with the potential to provide a high degree of discrimination in addition to classification. Since many of the float glasses have similar composition only techniques with a high analytical sensitivity providing measurements of good precision and a high level of accuracy can be used for achieving discrimination. The procedure using ICP-MS for analysis of glass fragments weighing as little as 300 µg offers the advantages of providing comprehensive, accurate and reproducible determination of major, minor and trace elements. By quantitative determinations of 30 elements a classification of float glass and complete discrimination of samples from all plants examined so far was possible. It is also possible to prove differences between successive batches of glass. However, it must be clarified through further experiments at what point in the production process do measurable differences in the elemental concentrations in glass occur, or in other words how large a piece of glass will be produced before reproducible analytical difference may be expected to occur."[1]

Results & Discussion

The technique of ICP-MS has been employed at the inorganic material analysis unit of the Forensic Science Institute of the Bundeskriminalamt since 1992. In 1996 an infrared (IR) laser ablation system was installed. Based on its insufficient performance, this system was replaced by an UV laser ablation system in 1997. This 266 nm UV laser ablation system was used until 2004 when it was replaced by a 213 nm UV laser ablation system.

The merits of solid sampling by LA-ICP-MS have been reported since the early nineties[2;3,4]. This

method has the following advantages:

- minimum amount of sample required (practically non-destructive)
- minimal sample preparation required - high savings of time/money
- greatly reduced problems with contamination
- less spectral interferences
- allows analysis of samples that are difficult or impossible to digest
- provides additional information, for example, the lateral distribution of elements in the sample

Recent review articles also cover the field of LA-ICP-MS in glass case work[5,6].

During the last ten years several projects have been carried out that helped us in our task to apply LA-ICP-MS in routine case work.

1.) International validation project on the comparability of the results of different LA-ICP-MS configurations for the analysis of glass

2.) Design of a common protocol for the investigation of (float) glass samples; application of time resolved analysis software for the interpretation of LA-ICP-MS measurements

3.) Production of a matrix matched standard for float glass analysis

4.) Validation of the method in accordance to ISO/IEC 17025 standards

5.) Establishment of a systematic and effective procedure for the interpretation of LA-ICP-MS results in glass case work / Evaluation of match criterion

Each topic will be discussed briefly below.

1.) International validation project on the comparability of the results of different LA-ICP-MS configurations for the analysis of glass

Within the NITE-CRIME (Natural Isotopes and Trace Elements in Criminalistics and Environmental Forensics) European Network, various forensic glass samples were analyzed in different laboratories using individual Laser Ablation Inductively Coupled Plasma Mass

Spectrometry (LA-ICP-MS) systems. The main objective of the interlaboratory tests was to cross-validate the different combinations of laser ablation systems with different ICP-MS instruments. A first study using widely distributed samples, such as the NIST SRM 610 and NIST SRM 612 reference glasses, led to deviations in the determined concentrations for trace elements amongst the laboratories up to 60 %. Extensive discussion among the laboratories and the production of new glass reference standards (FGS 1 and FGS 2) established an improved analytical protocol, which was tested on a well-characterized float glass sample (FG 10-1 from the BKA Wiesbaden collection). Subsequently, interlaboratory tests produced results for nearly all elements with a deviation < 10 %, demonstrating that LA-ICP-MS can deliver absolute quantitative measurements on major and trace elements for forensic and other purposes[7].

2.) **Design of a common protocol for the investigation of (float) glass samples**

Resulting from the particular NITE-CRIME activities (2001-2005) a protocol for the quantitative analysis of float glass was established. All results of the collaborative exercises were achieved by measuring glass fragments embedded in resin (Heraeus Kulzer Technovit 2000®). In contrast to the quantification of results achieved by aqueous solution ICP-MS measurements, the quantification of LA-ICP-MS measurements is calculated by using commercially-available time resolved software such as Glitter™. The advantage of displaying mass specific signals in form of a chromatogram is that additional information such as the lateral distribution of elements in the sample or the presence of spikes can be obtained. The protocol was published in 2005[7]. This NITECRIME protocol for glass analysis has also been published elsewhere[8]. Based on the ongoing development and referring to the special needs/circumstances in forensic case work (i.e. analysis of fragments) a sophisticated protocol has been produced by our group. This protocol is the basis for a common European protocol, which will be published in late 2007. The Paint & Glass expert working group of the European Network of Forensic Science Institutes (ENFSI) is in the final stage of releasing a Best

Practice Manual For Forensic Glass Examination. Appendix F of this document will describe the "Elemental Analysis of Float Glass by Laser Ablation-Inductively Coupled Plasma -Mass Spectrometry (LA -ICP-MS)". At the next annual meeting in September 2007 members of the ENFSI Paint & Glass Group will vote on this document.

3.) Production of a matrix matched standard for float glass analysis

To improve the accuracy of the quantitative analysis of float glasses by LA -ICP-MS, two matrix-matched standards were produced[7,9]. These forensic float glass standards (FGS) resemble soda-lime glass composition, but vary in their concentration of doped elements by a factor of 5. The concentration ranges of the doped elements were chosen according to their expected abundances based on the results of quantitative analysis of 61 float glasses of global origin by ICP-MS. Due to their discriminating power for forensic applications, the elements Al, K, and Fe were selected as minor elements and Li, Ti, Mn, Rb, Sr, Zr, Sn, Ba, La, Ce, Nd, Hf, and Pb were chosen as trace elements in varying concentrations[10]. Concentrations of these two glasses were published in 2005[7]. Further measurements from external laboratories enabled us to come up with improved mean values and standard deviations, which will be published in the near future.

4.) Validation of the method in accordance to ISO/IEC 17025 standards

To our knowledge the Netherland Forensic Institute was the first forensic institution that received ISO/IEC 17025 accreditation for a method that employed LA -ICP-MS for glass analysis[11]. The validation report can be downloaded from the institute website[12]. At the Forensic Science Institute of the BKA/Germany a method applying LA -ICP-MS for quantitative glass analysis achieved ISO/IEC 17025:2005 accreditation in May 2007. Based on the extensive validation work (referred to below) it can be used for routine case work.

5.) Establishment of a systematic and effective procedure for the interpretation of LA-ICP-MS results in glass case work / evaluation of match criterion

Results from the following smaller studies were taken into consideration for this issue:

A) Assessment of the variation of elemental concentrations in a single float glass pane

In association with the FBI, one randomly chosen commercially available float glass pane (48'' x 48'') was tested for its homogeneity concerning elemental concentrations and refractive index.

Figure 1: Sampling strategy on a single float glass pane

The pane was cut into 144 pieces (sample preparation was carried out by FBI laboratory). In total 34 of these pieces were chosen for homogeneity measurements. As shown in figure 1 33 pieces (see green triangle) and one additional piece (sample 104) which was examined on each of the eleven measurement days were selected. Therefore, 44 datasets with mean values of six replicate measurements of 19 elemental concentrations for fragments originating from the same float glass pane were obtained.

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No systematic changes of elemental concentrations were found throughout the sheet. The relative standard deviation for the 264 measurements (six replicates of 44 samples) range between 1,4 % (iron) and 7,3 % (hafnium). The effect of the sampling size on the precision for each element was examined by comparison of results of LA-ICP-MS measurements with inductively coupled plasma optical emission spectroscopy (ICP-OES) data (FBI) obtained after liquid digestion. Under the given experimental parameters a significant contribution of the sampling size (= micro heterogeneity issues) to the degree of variation for LA-ICP-MS results were found for some elements such as zircon, aluminum and hafnium.

B) Assessment of the variation of elemental concentrations in different float glasses

63 float glasses from different countries, manufacturers, production lines, but also glasses from the same production line with different pro duction dates were examined by LA -ICP-MS. Findings of this work are in good agreement with the results reported by Stoecklein[13] for liquid digestion ICP-MS measurements. It was found that major components Na, Ca and Mg show very small variation in different float glasses. K and Al show larger variations, but are highly correlated to each other. Based on trace element concentrations, a very good discrimination between float glasses can be achieved. In several cases, even glasses of the same color and thickness, produced in the same float glass line on different days could be discriminated from each other.

C) Evaluation of an appropriate match criterion for glass casework

Several strategies for the interpretation of comparative analysis of glass fragments by LA-ICP-MS are possible. Beside the quantification of glasses, comparative methods using a multivariate approach have also been worked out[14],[15]. We believe that quantification is the preferable procedure. In the first place, we think it is imperative at least to compensate for instrumental drift and mass bias changes during the measurements. Furthermore using a quantitative approach it is possible to compare the results with other independent techniques such as X-ray fluorescence analysis or inductively coupled plasma optical emission spectroscopy (ICP-OES).

For the interpretation of results of quantitative analysis from recovered and control glasses several statistical approaches are published[16],[17],[18],[19]. Hotellings T^2-Test, a multivariate equivalent of Student's t-test, as advocated by statisticians[20] proved to be impractical for our needs, since the number of factors (replicate measurements on the control sample plus replicate measurements on the recovered sample) must be at least by 2 higher than the number of dimensions (i.e. number of elements, in our case 19). We also do not consider the Student's t-test an appropriate match criterion for our particular analytical

method, because we experienced an unacceptably high rate of false exclusions (Type I errors). Though we are aware of the "falling of the cliff" effect, we are considering the n-sigma criteria the best choice for our needs. For each element, we have defined an n-sigma range defined by a lower limit of [c(control) / (1 + n RSD)] and an upper limit of [c(control) x (1 + n RSD)] around the concentration (c(control) is the mean concentration value of six replicate measurements) of the control sample. If the mean concentration of the recovered sample falls into this range, the two concentrations are considered to be indistinguishable.

A further problem, which can lead to high rates of false exclusions, is the estimation of the measurement uncertainty. The standard deviation of six replicate measurements within one calibration set is unrealistically small and gives a wrong impression of the measurement uncertainty when comparing data from different calibration sets. Therefore, we estimated a system relative standard deviation (RSD) based on 90 determinations (six replicate measurements) of the concentrations of the 19 elements in the German glass standard DGG 1 (Deutsche Glastechnische Gesellschaft, Offenbach/Germany). The system RSD was set to be at least 3 %.

Based on the 44 data sets of 19 elemental concentrations of a single float glass pane (946 pairwise comparisons) and based on the 63 data sets from float glasses of different origin (1953 pairwise comparisons), an appropriate match criterion for routine glass casework was developed.

In figure 2 results for test calculations for the number of type I and type II errors are displayed for a number of varying match criteria.

Starting on the left type I and type II errors are calculated using a match criterion of 2 sigma (system standard deviation, n=2) under the condition that 0 significantly differing element concentrations are accepted (m= 0). This results in an unacceptably high rate of type I errors (~52 %). On the right type I and type II errors are calculated using a match criterion of 20 sigma (system standard deviations, n=20)

under the condition that 6 significantly differing element concentrations are accepted (m= 6). This of course results in an unacceptably high number of type II errors (~28 %).

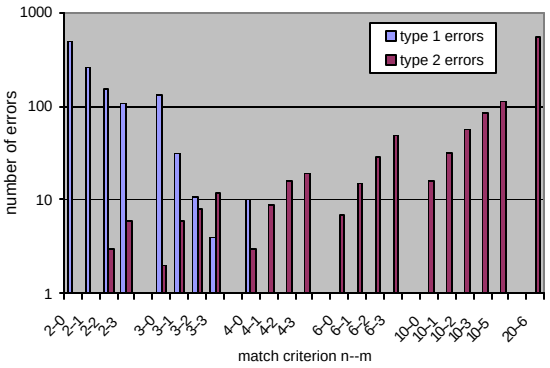

Figure 2: Calculation of type I & type II errors for several sets of match criteria (n = number of system standard deviations; m= number of excluded elements)

As can be clearly seen a good compromise of low type I and type II errors are achieved by a 4-0 setting (four sigma intervals under the condition that no significantly differing element concentrations are accepted).

By calculation with the 44 data sets (from the IFBI-glass) resulting in 946 pairwise comparisons only 10 type I errors occurred (1,06 %). By calculation with the 63 data sets from different float glasses (1953 pairwise comparisons) only 3 type II errors occurred (0,15 %).

Certainly the VBA macro can not replace the glass examiners expertise, but is only used to get a first impression of the data. Further aspects have to be considered as well, e.g. high tin concentrations occurring on the outer surfaces of float glasses etc.

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