Application Note #1901

TRACER 5 Sensitivity

Introduction

The purpose of this study is to determine the sensitivity of the Bruker TRACER 5 family of instruments in the various configurations available. Data is presented for the comparison of the TRACER 5g, which is based on a 1 µm graphene window detector, with the TRACER 5i, which is based on an 8 µm beryllium window detector. Data is presented for the use of helium, vacuum and air environment. The elements of interest for this study are the very low atomic number elements such as sodium, magnesium, and aluminum[1]. The energy of the X-rays generated by these elements is very low (Na – 1,041 eV; Mg – 1,253 eV; Al – 1,486 eV) and thus are readily absorbed by any material between the sample and the detector chip. The absorbers might include the air path, the detector window and the instrument window. Any modification of materials between the sample and detector chip can greatly affect the sensitivity of the measurement.

The general conclusion of this study indicated that the use of a graphene window detector vs. a beryllium window detector will improve the sensitivity for Na by a factor of about 3 and for Mg by a factor of about 2. The use of a helium atmosphere with no window will improve the sensitivity for Mg by more than a factor of 10 and even more for Na. Limits of detection for Na on a TRACER 5g using He with no window are on the order of 300 ppm and for Mg are on the order of 125 ppm.

[1] Silicon (Si) also emits a low energy X-ray (1,740 eV) and thus will benefit from modified windows and atmosphere, however, the standards used in this study were silicon based, therefore, it was not possible to determine the sensitivity for Si. In addition, phosphorous, sulfur and chlorine will have some benefit from the modified windows and atmosphere.

Method

In this study a series of standards was measured in each configuration tested. The data was taken using Bruker Artax software. Once all the data was taken for each configuration, it was processed as described in Appendix B. The results calculated were the Limit of Detection and the sensitivity for each element. Limit of detection (LOD), is the minimum concentration at which the presence of the element can be detected. In the field of XRF, the LOD is the concentration that when detected has a 50% chance of being present. It is defined as the concentration associated with the intensity at zero concentration plus three standard deviations. Here this value is expressed in parts per million (ppm). A smaller LOD means that lower concentrations of the element can be measured using that configuration. The sensitivity of the configuration represents the number of counts which reach the detector for an element within the measurement time per unit concentration. In this case the value is expressed as counts/ppm during the 60 sec measurement time. Larger values of sensitivity indicate that more X-rays are arriving at the detector thus resulting in improved measurement and lower limits of detection.

The same excitation conditions were used for all the configurations so that comparison of the data was not complicated by using different currents. In many of the configurations it may be possible to achieve better (lower) limits of detection by using higher currents and thus achieving higher count rates.

Configuration: Air; 3µm Prolene Window

This configuration is the normal configuration for operation of the TRACER 5. That is an air path was used along with the normal protective window of 3 µm Prolene on the front of the instrument. The results were:

Table A: Air path & Prolene Window

TRACER 5g

	LOD (PPM)	Sens (counts/PPM)
Na	N/A	N/A
Mg	932	0.12
Al	462	0.59
Ca	25	13.13
Fe	46	29.36

TRACER 5i

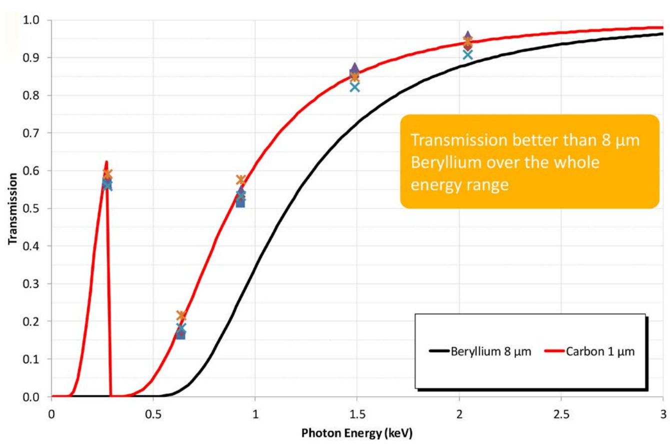
	LOD (PPM)	Sens (counts/PPM)
Na	N/A	N/A
Mg	1490	0.08
Al	515	0.49
Ca	26	14.42
Fe	45	32.52

The highest sodium content in the standard set was 3.1% and the measurements could not distinguish that from the background, indicating that the LOD for Na in both configurations is greater than 3%. Other measurements indicate that the Na LOD for the TRACER 5g in this configuration is between 5% and 10%.

This data clearly demonstrated the improvement in sensitivity for the light elements Mg and Al resulting from the graphene window on the detector. This is as expected given the transmission curves for the detector windows:

Figure 1: Transmission of Be and Graphene Window

Mg X-ray at 1.25 kV; Al X-ray at 1.49 kV



The results for the Ca and Fe are not changed much by using the graphene window. The Ca X-ray is at 3.69 keV while the Fe X-ray is at 6.40 keV. As the graph above indicates, the transmission of the graphene window is almost the same as the beryllium window at these energies. Thus, the values of sensitivity should be similar. In fact, the sensitivity for the TRACER 5i is slightly higher for Fe than that for the TRACER 5g. This is a result of instrument to instrument variability, not of any difference in the configuration.

Configuration: Helium, No Instrument Window

In this test the Prolene window was removed from the instrument and laboratory-grade helium flowed through the front end of the instrument at 0.6 l/min[2]. In this configuration the instrument must be used in a nose-down configuration (see Appendix A for details) as shown in Figure 2.

Figure 2: TRACER 5i in nose-down configuration

This is to ensure that foreign matter does not fall into the instrument causing contamination. Removing the contamination is difficult as it might damage delicate components located in that area.

Air is composed largely of nitrogen (N) and oxygen (O), in addition, other gases are present such as argon (Ar). These gases can stop the transmission of low energy X-rays, such as those from sodium and magnesium. Replacing those gases with He dramatically increased the transmission of the light element X-rays, thus, substantially increasing the sensitivity of the measurement. This configuration gives the maximum sensitivity of all the configurations tested. The results were:

Table B: Helium, No Instrument Window

TRACER 5g

	LOD (PPM)	Sens (counts/PPM)
Na	312	0.62
Mg	122	2.13
Al	134	4.41
Ca	24	14.04
Fe	50	25.87

TRACER 5i

	LOD (PPM)	Sens (counts/PPM)
Na	828	0.20
Mg	185	1.17
Al	177	3.08
Ca	22	16.10
Fe	48	30.03

[2] Additional work using the helium flow has indicated that the actual flow rate can be as low as 0.1l/min; if the flow is maintained the rate has little impact.

These results clearly indicate the dramatic impact of using helium. The sensitivity for Mg is improved by well over an order of magnitude (e.g. 2.13 c/ppm for He/No window vs. 0.12 c/ppm for Air/Prolene in the TRACER 5g). In the case of Na, the improvement is substantially greater as the energy is lower and thus the difference in absorption will be greater. This configuration results in a Na limit of detection of 312 ppm for the TRACER 5g and 828 ppm for the TRACER 5i. Slightly better limits of detection can be achieved by using lower excitation voltage, and LOD's as low as 275 ppm have been observed using 10 kV excitation.

Configuration: Balloon He; no Prolene Window

In this test the Prolene window was removed and Balloon He was flowed through the front end at 0.6 l/m. Like the laboratory He configuration, this configuration requires that the instrument be operated in the nose down configuration to avoid contamination of the front end of the instrument.

Balloon helium is the helium which is sold at may party and department stores for filling party balloons. The composition of balloon helium is not well controlled and typically contains around 20% air. This air causes the transmission of low energy x-rays to be reduced when compared to that achieved using laboratory helium. The results were:

Table C: Balloon He, No Instrument Window

TRACER 5g

	LOD (PPM)	Sens (counts/PPM)
Na	356	0.52
Mg	127	1.95
Al	143	4.07
Ca	25	14.15
Fe	50	26.36

TRACER 5i

	LOD (PPM)	Sens (counts/PPM)
Na	953	0.17
Mg	200	1.06
Al	189	2.85
Ca	21	16.13
Fe	47	30.43

The air in the balloon helium causes a 16% drop in sensitivity for Na in the TRACER 5g (0.52 c/ppm for balloon He vs 0.62 c/ppm for laboratory He) and an 8% decrease in sensitivity for Mg (1.95 c/ppm for balloon He vs. 2.13 c/ppm for laboratory He). In addition, as balloon He is not well defined, the transmission of the low energy X-rays may vary from one container of balloon He to another. When using quantitative calibrations, this change in sensitivity can be corrected by using the Type Standardization feature available in the TRACER 5 software.

It is important to note that all Bruker factory helium atmosphere calibrations are performed using laboratory helium. Thus, if balloon He is used in conjunction with a factory calibration the quantitative results for the light elements in the calibration will be seriously impacted. The results in this case will be substantially below the actual values of the samples. This error can be corrected by measuring several standards with the elements of interest and calculating the appropriate coefficients for Type Standardization. Due to the variability of balloon helium from one tank to the next, best results will be obtained by calculating the coefficients for Type Standardization for each tank of balloon He used.

Configuration: Helium; 3µm Prolene window

When it is not possible to use the instrument in a nose down configuration it is possible to use the helium environment with the 3 µm Prolene window. This can be achieved by leaving a corner of the window slightly open and flowing the helium through the instrument just like when no window is present. In this case the results are:

Table D: Helium, Prolene Window

TRACER 5g

	LOD (PPM)	Sens (counts/PPM)
Na	548	0.31
Mg	155	1.44
Al	165	3.36
Ca	27	14.00
Fe	50	26.40

TRACER 5i

	LOD (PPM)	Sens (counts/PPM)
Na	1673	0.09
Mg	255	0.75
Al	217	2.26
Ca	26	15.23
Fe	48	29.83

In this case the transmission of the window reduces the sensitivity of the TRACER 5g for Na by 50% (0.31 c/ppm for system with prolene window vs. 0.62 c/ppm for the system with no window) and for Mg by 32% (1.44 c/ppm for system with prolene window vs. 1.44 c/ppm for the system with no window).

Configuration: Vacuum, gridded vacuum window

This configuration is the standard vacuum configuration for the TRACER 5. In this case the gridded vacuum window is installed on the unit and the portable vacuum pump is attached to the instrument as shown in Figure 3. A vacuum of less than 5 torr is achieved in a few minutes and is maintained throughout the experiment. The results were:

Table E: Vacuum, Gridded Window

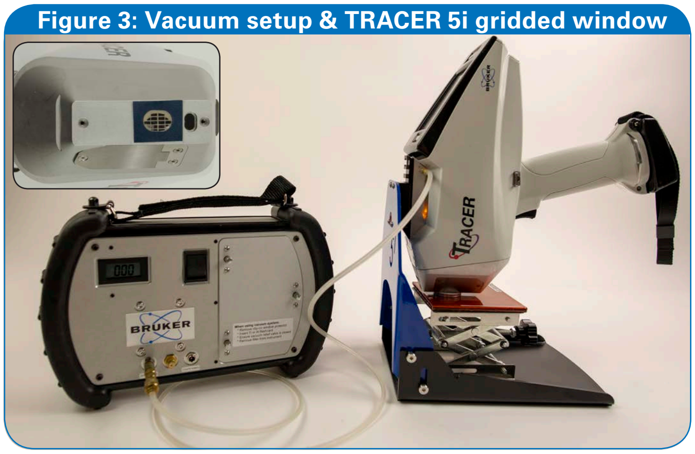
TRACER 5g

	LOD (PPM)	Sens (counts/PPM)
Na	1643	0.08
Mg	307	0.53
Al	345	1.23
Ca	52	8.86
Fe	52	24.59

TRACER 5i

	LOD (PPM)	Sens (counts/PPM)
Na	6321	0.02
Mg	541	0.27
Al	323	0.94
Ca	44	9.60
Fe	53	26.19

Figure 3: Vacuum setup & TRACER 5i gridded window



In this case the sensitivity improvement for Mg is a factor of 3-4 when compared to the sensitivity when using air (for the TRACER 5g 0.53 c/ppm in vacuum vs 0.12 c/ppm in air). While these results are not as dramatic as those achieved using a helium environment, they are still substantially better than the normal configuration using air. The advantage of this configuration is that it can be achieved without the need for compressed gas and with a completely portable system.

In this test the sensitivity and limit of detection of Ca is impacted by the presence of Ca in the vacuum window. The overall sensitivity of the mid-range elements will be impacted by the presence of the grid on the vacuum window. The grid will absorb some of the X-rays generated by those elements as can be seen by the 20% drop in sensitivity for Fe (for the TRACER 5g 24.6 c/ppm for vacuum vs 29.4 c/ppm for air).

Conclusions

- The sensitivity and limits of detection for sodium (Na) on the TRACER 5g with a graphene detector window are about three times better than the TRACER 5i with a beryllium detector window when a helium atmosphere is used (Compare the 5g results to the 5i results in Tables B, C, D).

- The sensitivity and limits of detection for magnesium (Mg) on the TRACER 5g are about two times better than the TRACER 5i when a helium atmosphere is used (Compare the 5g results to the 5i results in Tables B, C, D).

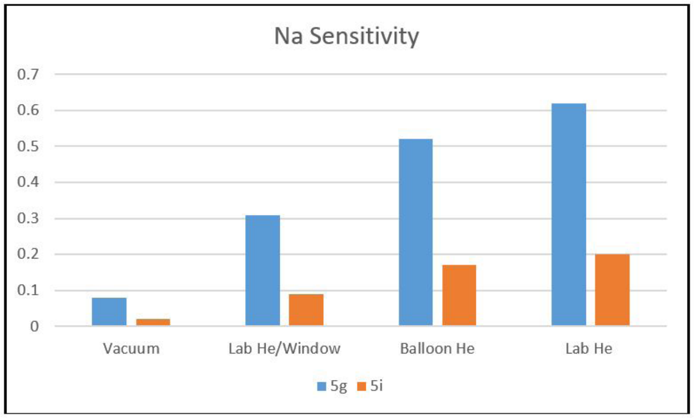
- The use of a laboratory helium atmosphere and no window results in almost an order of magnitude improvement in the sensitivity and limit of detection of Mg when compared to the standard window with air (Compare Tables B vs. Table A).

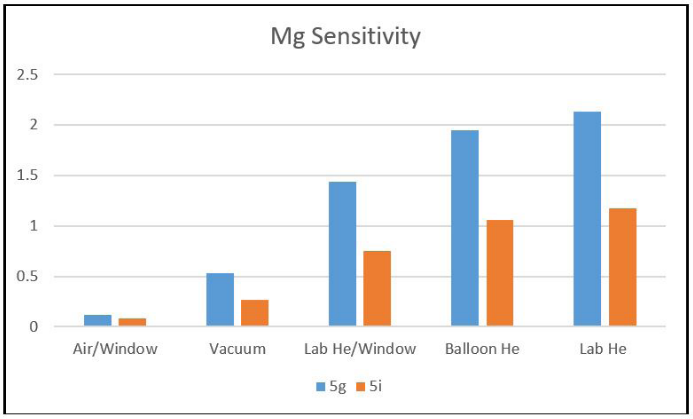
- The use of balloon helium atmosphere results in a reduction of the sensitivity for Na by about 15% and Mg by about 10% when compared to laboratory helium (Compare Table B vs. Table C). As the Mudrock He calibration is prepared using laboratory helium, the use of balloon helium will lead to incorrect results being calculated by that calibration. Appropriate Type Standardization will correct for this error.

- The presence of a single Prolene window reduces the sensitivity for Na by 50% and for Mg by 35% when compared to no window (Compare Table B vs. Table D).

- The use of vacuum improves the sensitivity and limit of detection for Al, Mg and Na. While the improvement is not as dramatic as the use of helium, this environment can be generated using a portable vacuum pump and does not require compressed gas to be used (Compare Table E vs. Table A).

- The environment and detector window have little or no effect at the energy of calcium (Ca) at 3,690 eV and higher. (Compare the Ca and Fe data in all the tables).





Appendix A

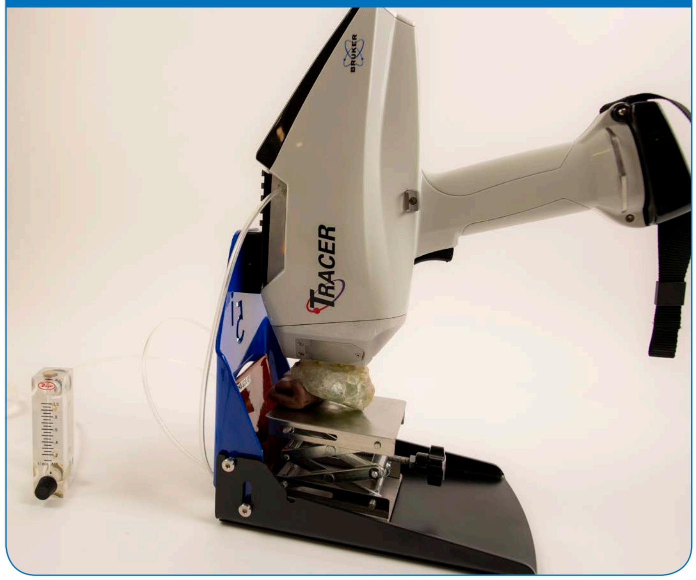
Operation of TRACER 5 in Nose Down Configuration

In order to achieve the maximum sensitivity with the TRACER 5, it is necessary to use a helium atmosphere and to remove the Prolene window on the front of the instrument. When this is done it is essential to use the instrument in a nose down configuration (Figure 2). This configuration minimizes the chance that any foreign material will enter the volume around the detector and other important mechanical parts. The presence of foreign material in the front end of the instrument and attempts to remove such material could damage the detector or the mechanics of the instrument.

The instrument should not be used without the Prolene window for anything other than solid materials like rocks and metal samples. Do not use the instrument in this configuration when measuring powder or liquid samples. Powder samples can be disturbed by the flow and there is a possibility that the powder could enter the front end of the instrument and cause damage. Liquid samples are dangerous, as it is possible that the liquid may evaporate and condense at the detector, which is cooled. This could lead to significant damage to the instrument.

When operating in a nose-down configuration, the best way to arrange the unit is to mount it in the desktop stand and raise the sample to the instrument using a scissor stand as shown in Figure 2. This allows the sample to be raised to meet the front of the instrument. In cases where the sample is not flat on both sides, molding clay is helpful in arranging the flat surface to be measured in the appropriate configuration (see Figure 4).

Figure 4: Molding clay used to help level the measurement surface



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