

G-probe 10 summary
June 2013
Stephen Wilson

A total of twenty five labs were provided samples for the G-probe 10 study. A total of eight LA-ICP-MS labs submitted data. The sample used in this study (GP-MAPS) was a synthetic apatite material ($\text{Ca}_3(\text{PO}_4)_2$) prepared at the USGS. GP-MAPS was developed using a USGS co-precipitation process which included the addition of sixty seven minor and trace elements. For calibration purposes a sample of USGS reference material MAPS-4 was provide, but participants had the option to use the calibration procedure of choice. In previous G-probe studies the element distribution figures displayed results from all participants. In this round of testing an outlier rejection step was used to eliminate results from one laboratory where their results differed from the average value by a factor of 5 to 10. Elements where outlier rejection was applied are denoted by an asterisk adjacent to the element in the figure title and table 2. If you have any questions or comments about this study please forward them to me at your earliest convenience.

Z-score evaluation:

Laboratory results are evaluated for accuracy using a Z-score approach. In this procedure a target concentration is determined using bulk methods of analysis at a minimum of two independent laboratories. Element concentrations not quantified using bulk methods of analysis may also be reported when study consensus values vary by less than 10%. The target standard deviation (H_a) for each element assessed was calculated from a modified form of the Horwitz function (equation 1).

$$1) H_a = k X_a^{0.8495}$$

Where X_a is the concentration of the element expressed as a *fraction*. The factor “k” is assigned a value of 0.02. Z-scores were calculated for each elemental result submitted by each laboratory using equation 2.

$$2) z = [X - X_a] / H_a$$

Where: X is the contributed result, X_a is the assigned value and H_a is the target standard deviation. Z-score results in the range $-2 < z < 2$ are considered to be 'satisfactory' (in the sense that no action is called for by the participant). If the z-score for any element falls outside this range, especially if it is outside the range $-3 < z < 3$, it would be advisable for the contributing laboratory to examine its procedures, and if necessary, to take action to ensure that determinations are not subject to unsuspected analytical bias.

Below you will find summary results for each element studied in this test. Target element concentrations were determined using a combination of bulk analysis and consensus study results. In element diagrams you will find information for each technique providing a value. Also included is the target value (◆) and calculated

precision ($X \pm Ha$) (\diamond) based on the Horwitz equation. A figure is also presented representing the data compilation for the entire study when more than one technique reported values. The study average is represented by \blacksquare , the standard deviation of the average by \blacksquare and the maximum and minimum values by \square . This study average is calculated primarily for the analysis of the major elements where multiple techniques provided data. For each technique an average value is presented (ex LA-ICP-MS, \blacktriangle) as well as \pm one standard deviation (ex LA-ICP-MS, \blacktriangle), and the maximum and minimum values reported (ex LA-ICP-MS, \triangle).

Table 1 Symbols used on figures 1 through 58

| <u>Symbol type</u> | | <u>Represents</u> |
|---------------------|---|--|
| Large solid symbol, | ● | Study or method average |
| Small solid symbol, | • | Study or method one standard deviation |
| Large open symbol, | ○ | Study or method Maximum or Minimum |

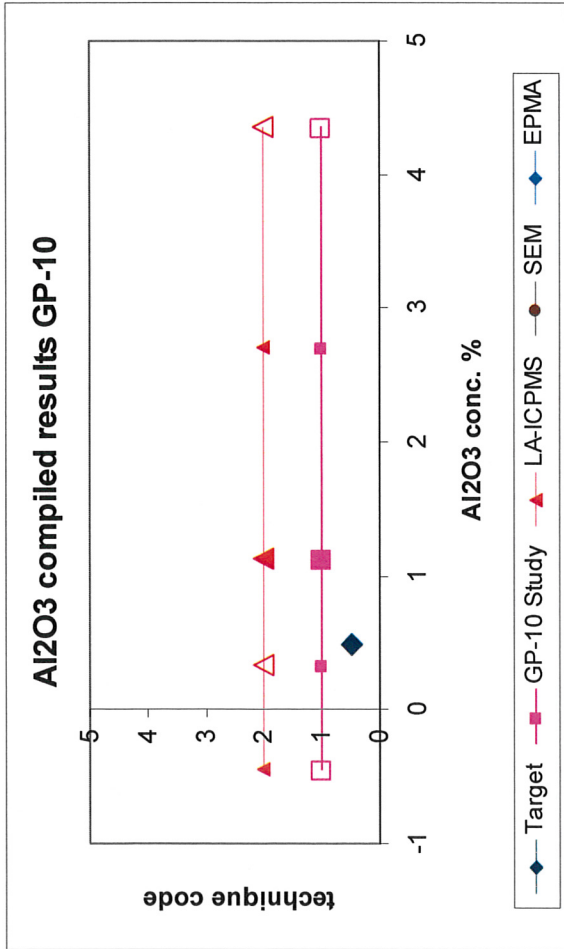


Figure 1. Al₂O₃ results for G-probe 10 study

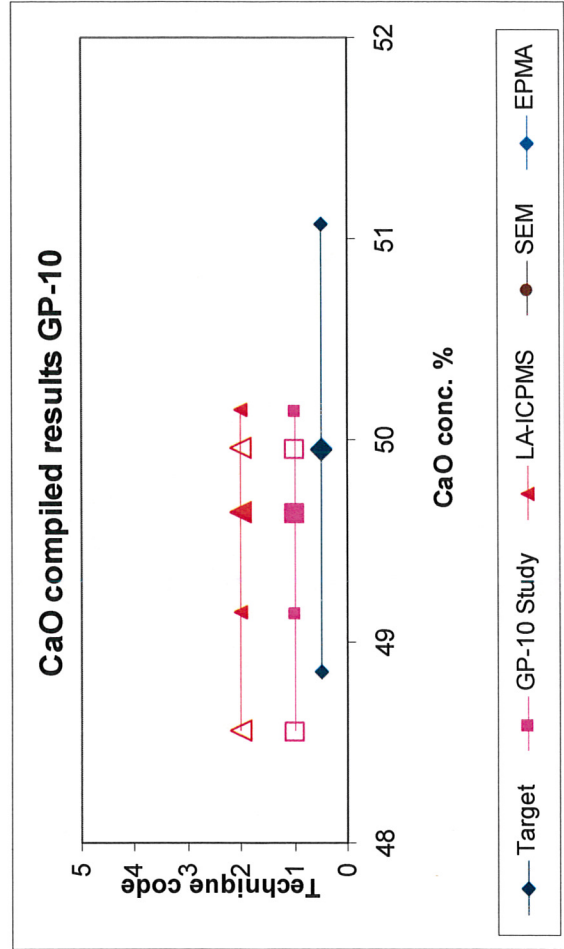


Figure 2. CaO results for G-probe 10 study

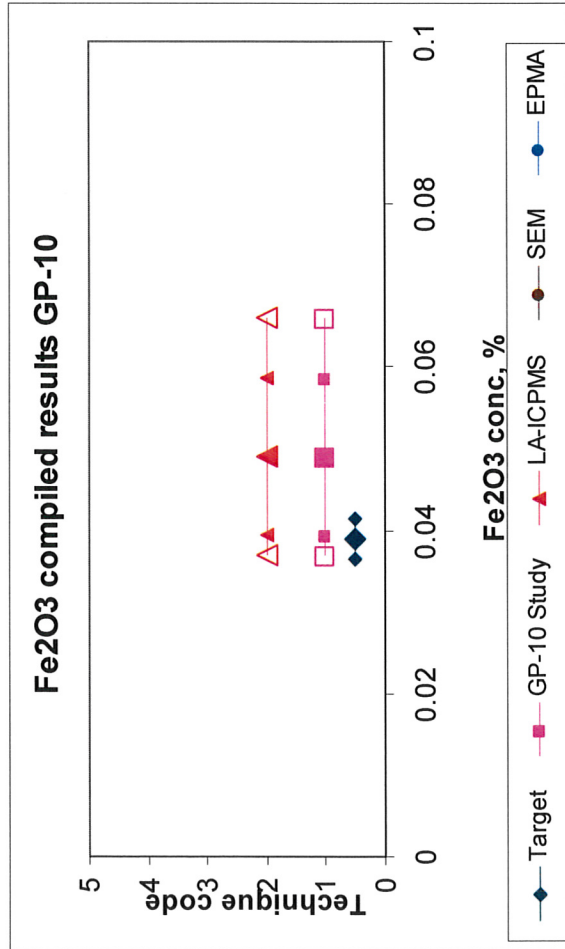


Figure 3. Fe₂O₃ results for G-probe 10 study

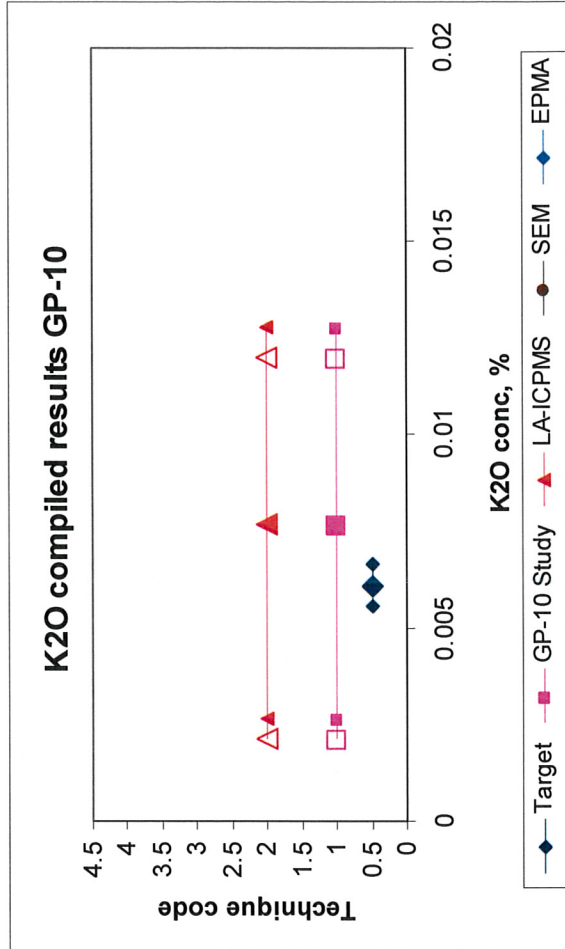


Figure 4. K₂O results for G-Probe 10 study

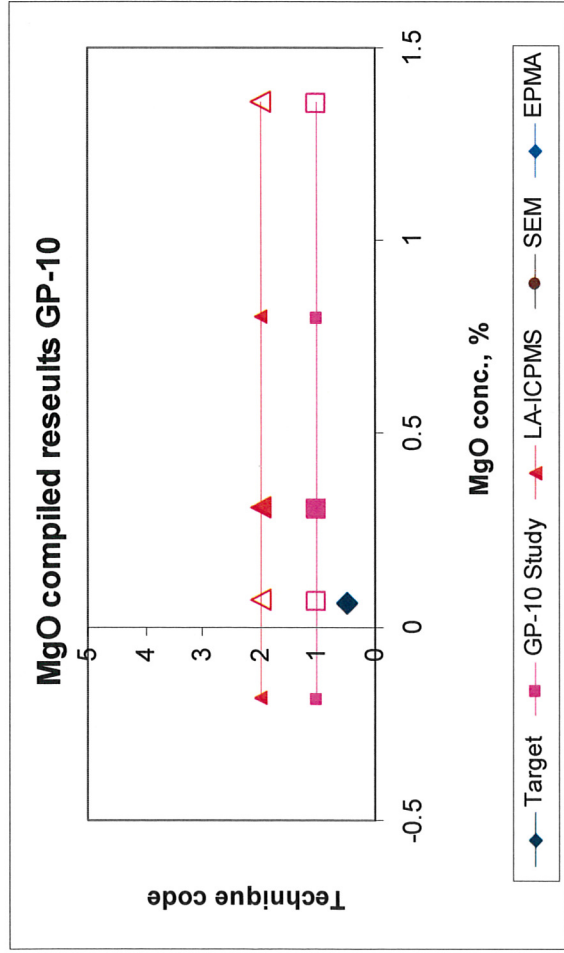


Figure 5. MgO results for G-probe 10 study

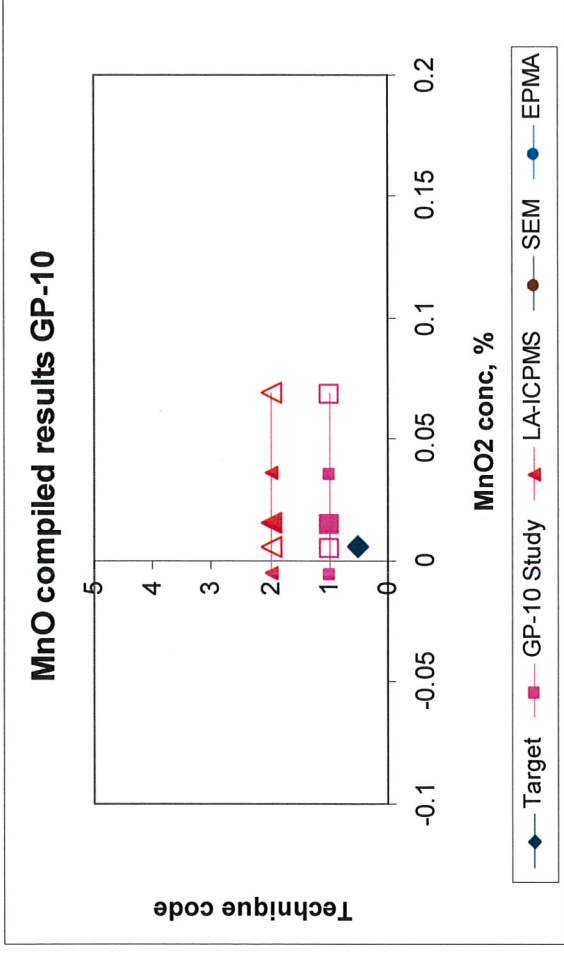


Figure 6. MnO₂ results for G-probe 10 study

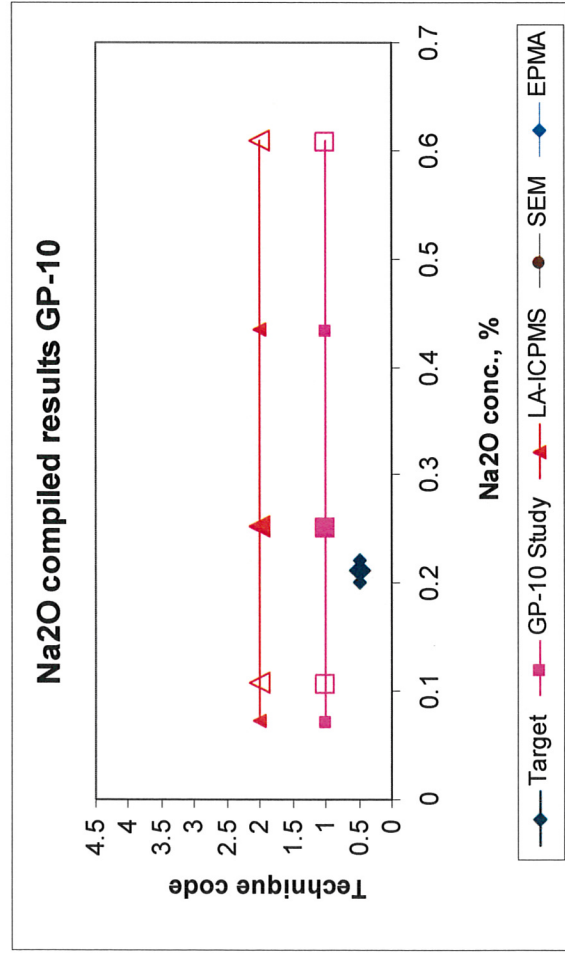


Figure 7 Na₂O results for G-probe 10 study

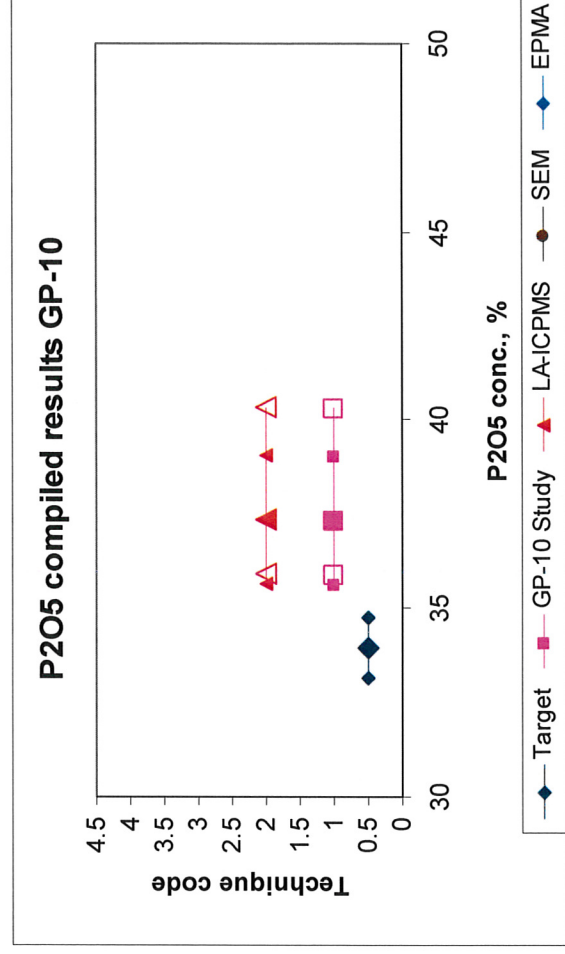


Figure 8. P₂O₅ results for G-probe 10 study

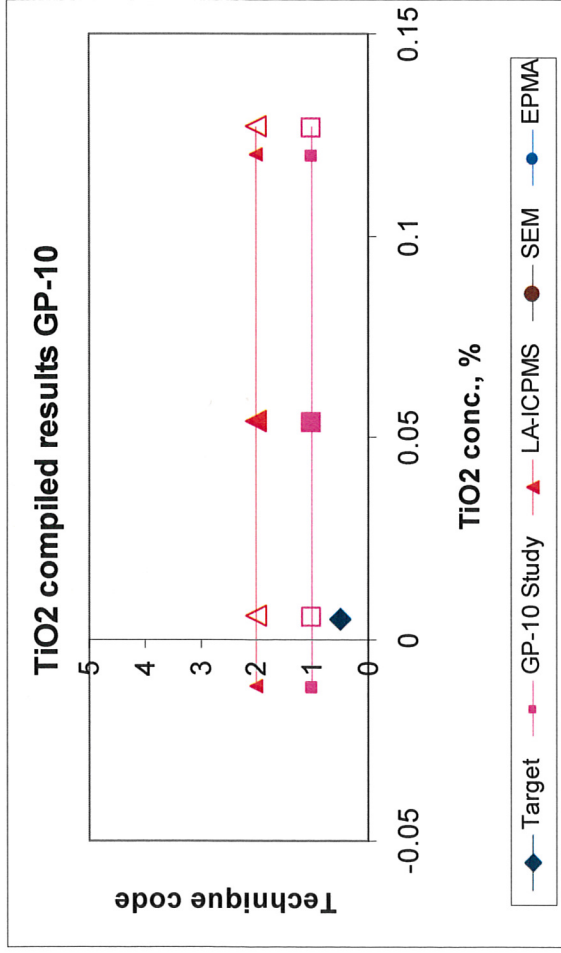


Figure 9. TiO₂ results for G-probe 10 study

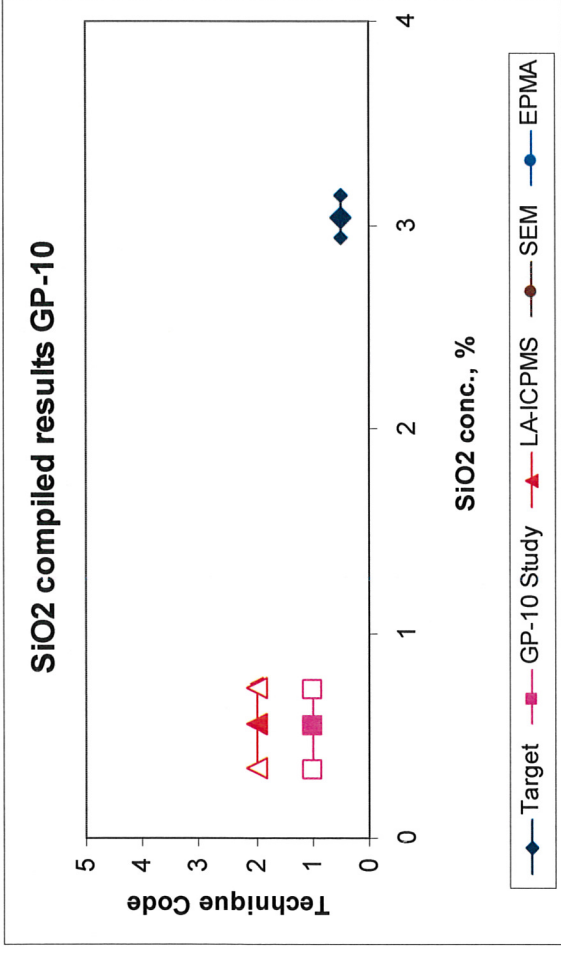


Figure 10. SiO₂ results for G-probe 10 study

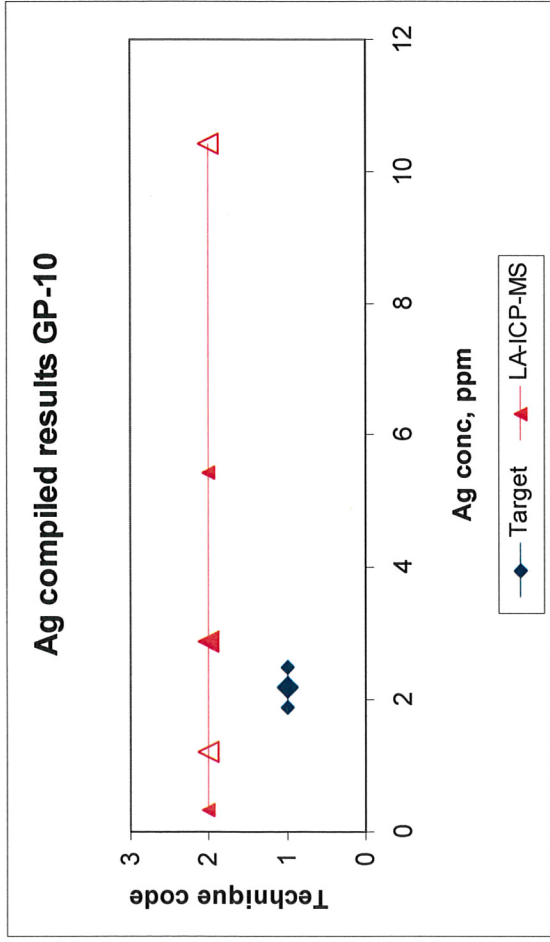


Figure 11. Ag results for G-probe 10 study

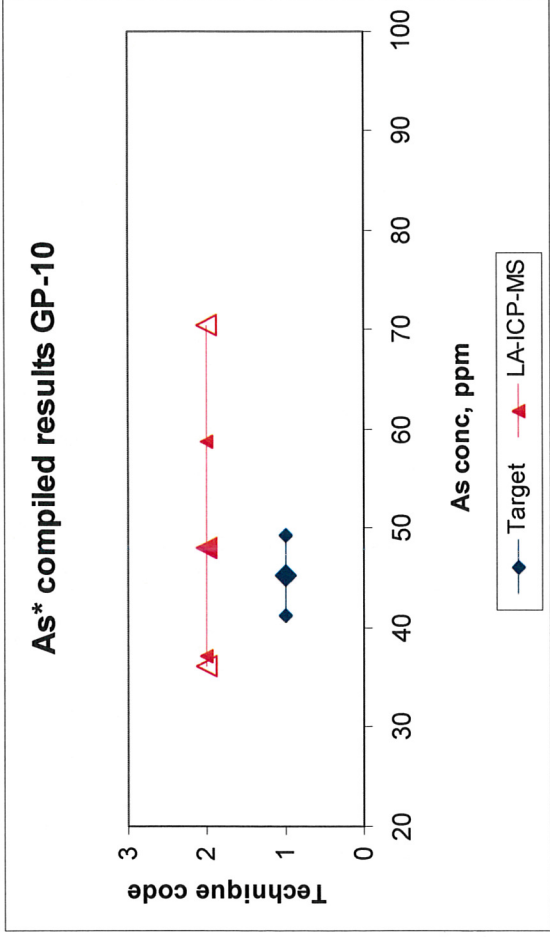


Figure 12. As results for G-probe 10

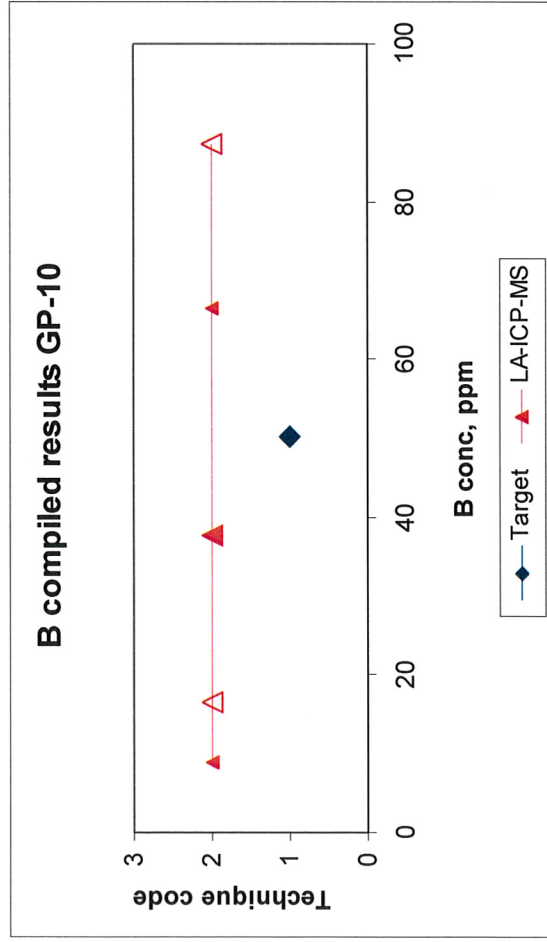


Figure 13. B results for G-probe 10

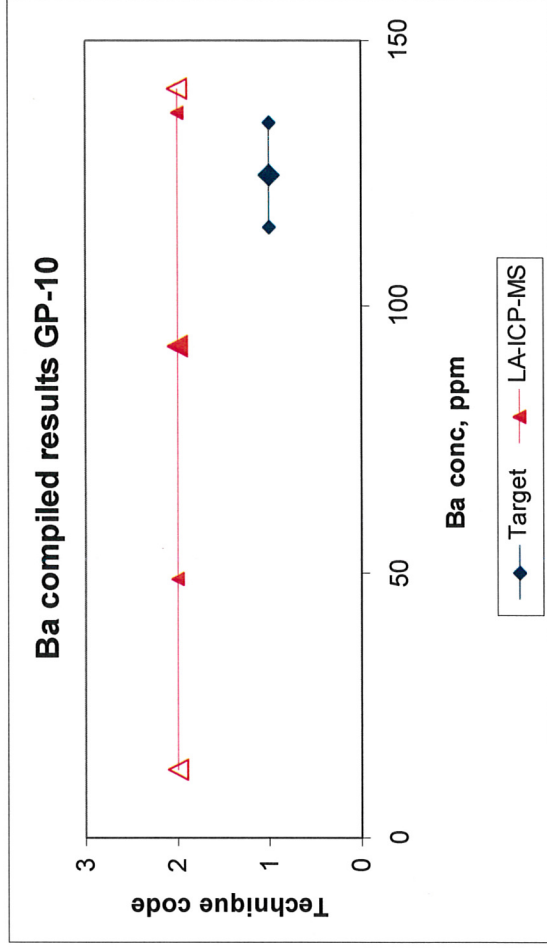


Figure 14. Ba results G-probe 10 study

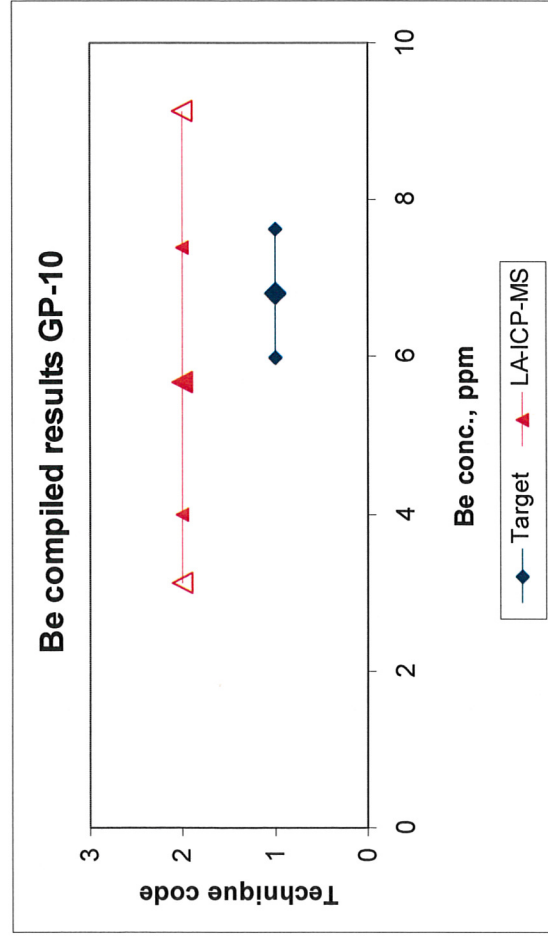


Figure 15. Be results G-probe 10 study

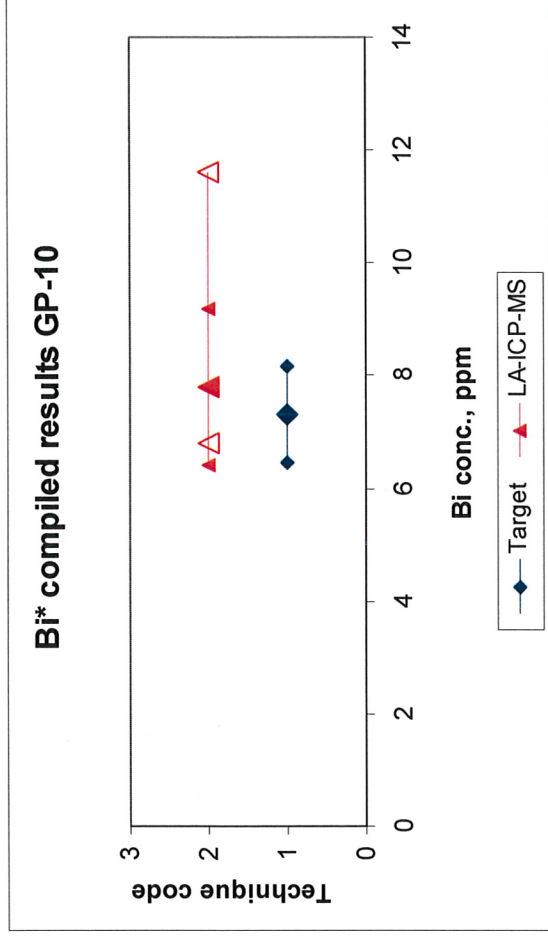


Figure 16. Bi results G-probe 10 study

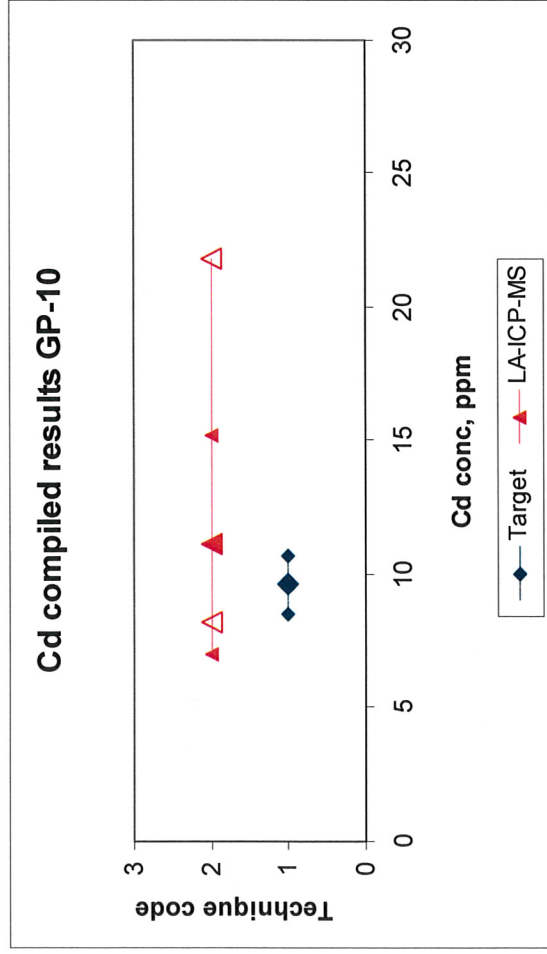


Figure 17. Cd results G-probe 10 study

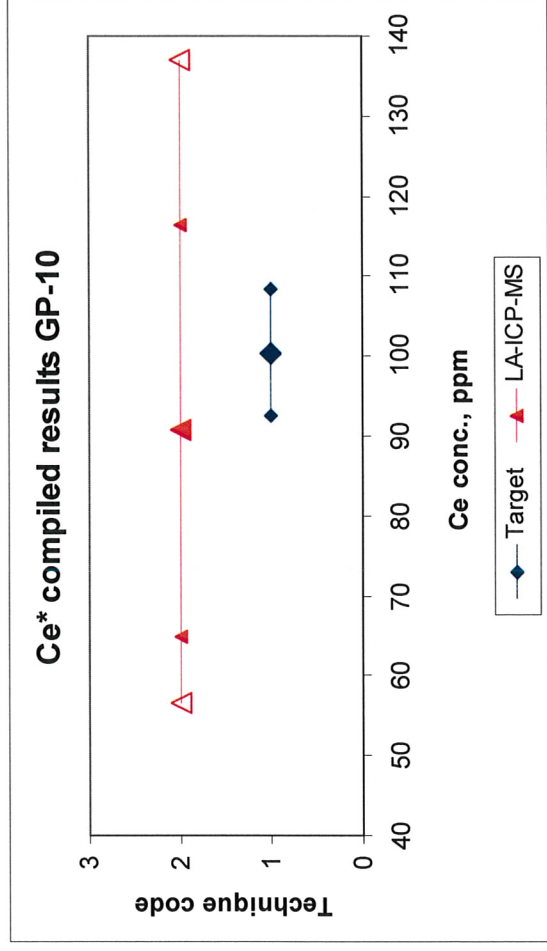


Figure 18. Ce results for G-probe 10 study

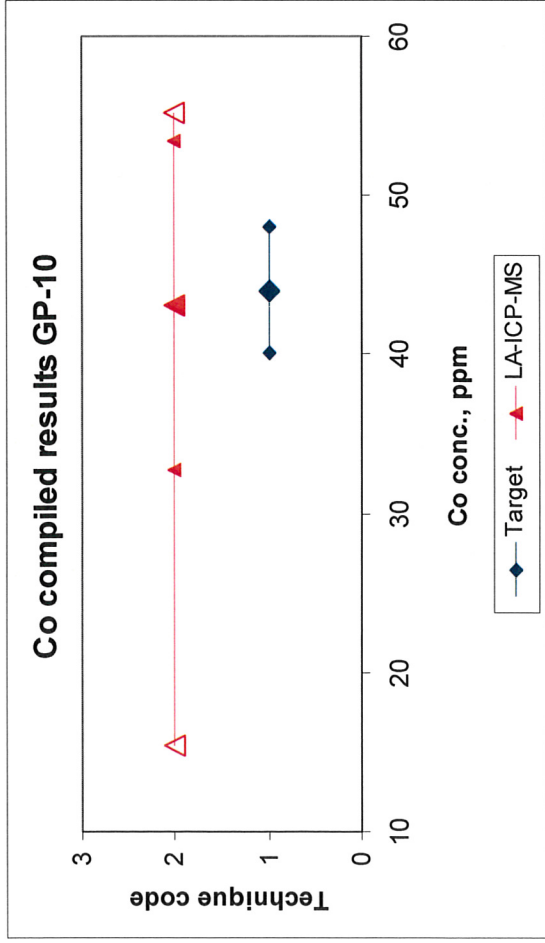


Figure 19. Co results for G-probe 10 study

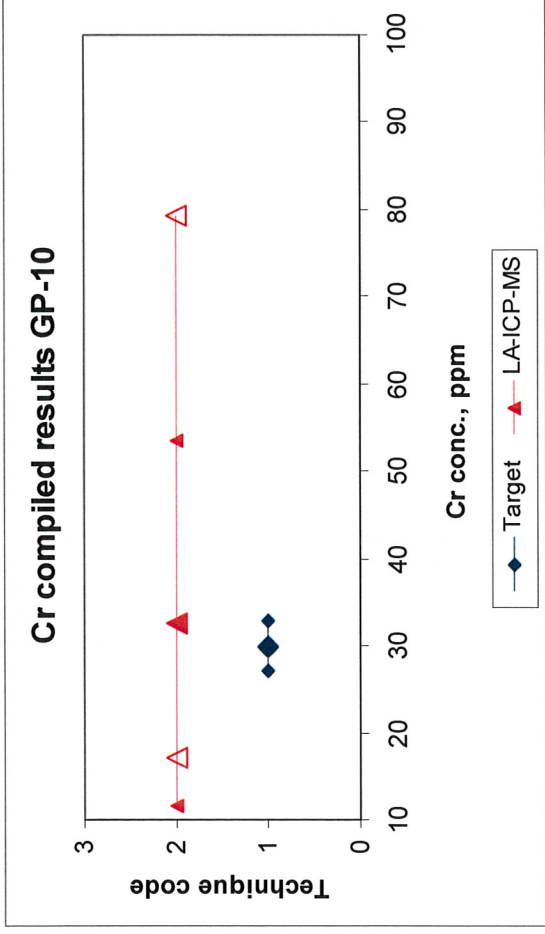


Figure 20. Cr results G-probe 10 study

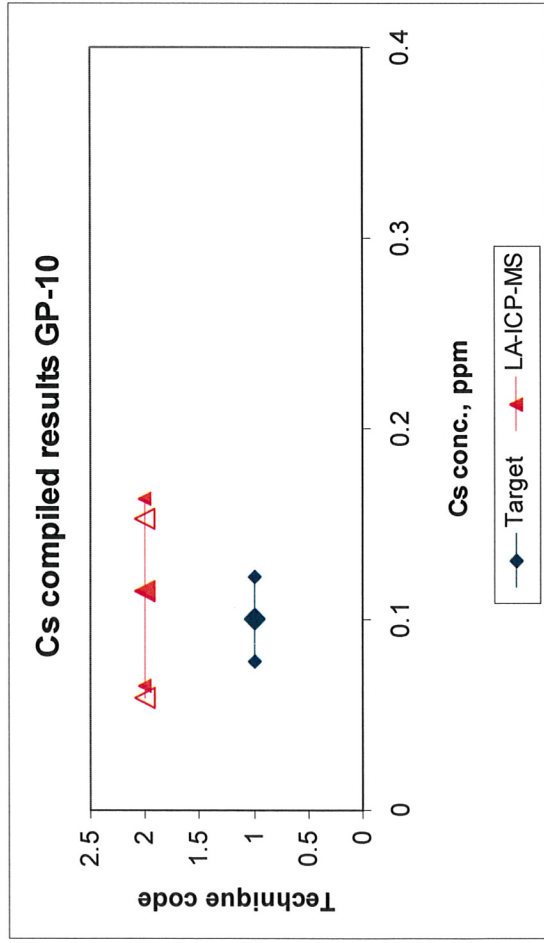


Figure 21. Cs results G-probe 10 study

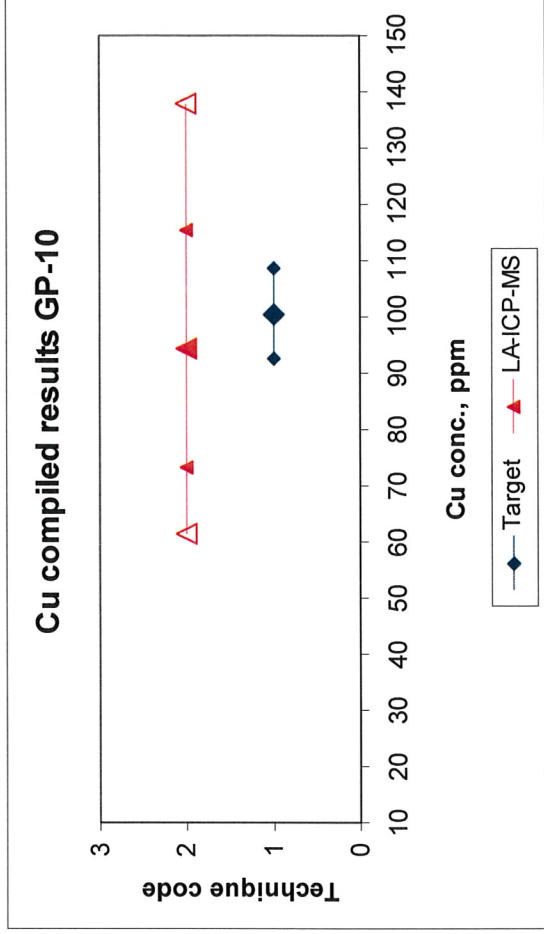


Figure 22. Cu results G-probe 10 study

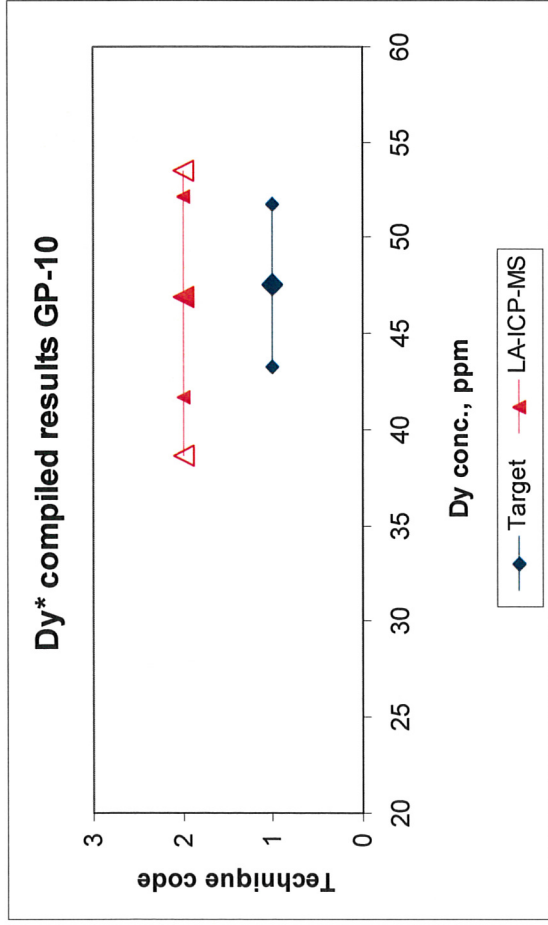


Figure 23. Dy results G-probe 10 study

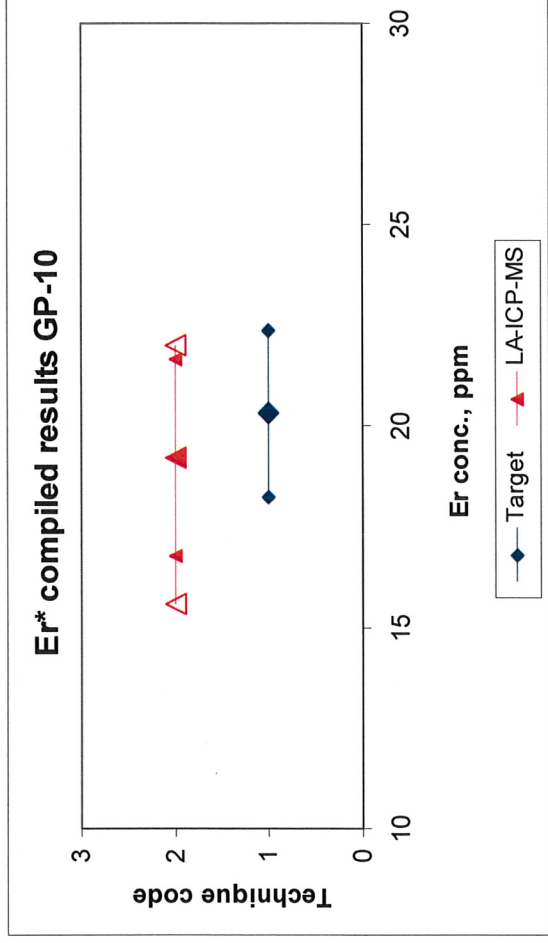


Figure 24. Er results G-probe 10 study

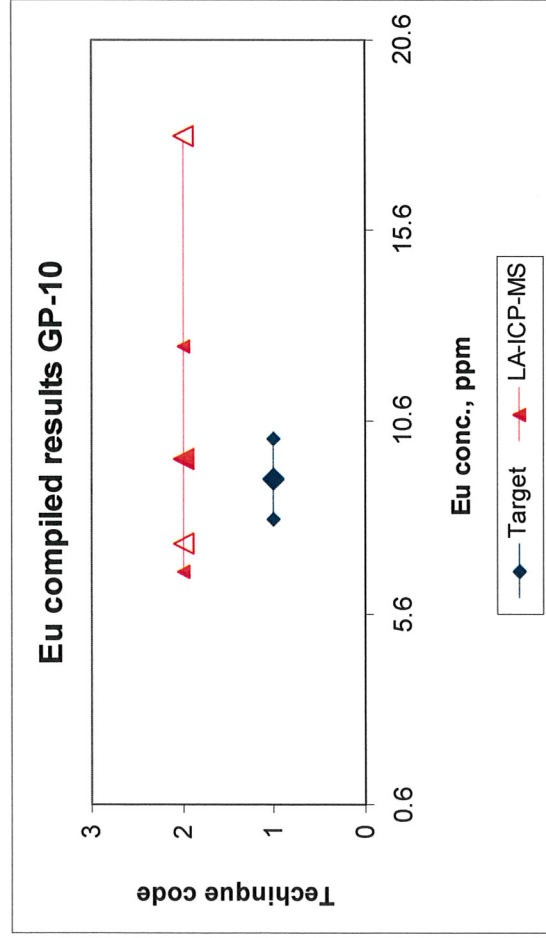


Figure 25. Eu results G-probe 10 study

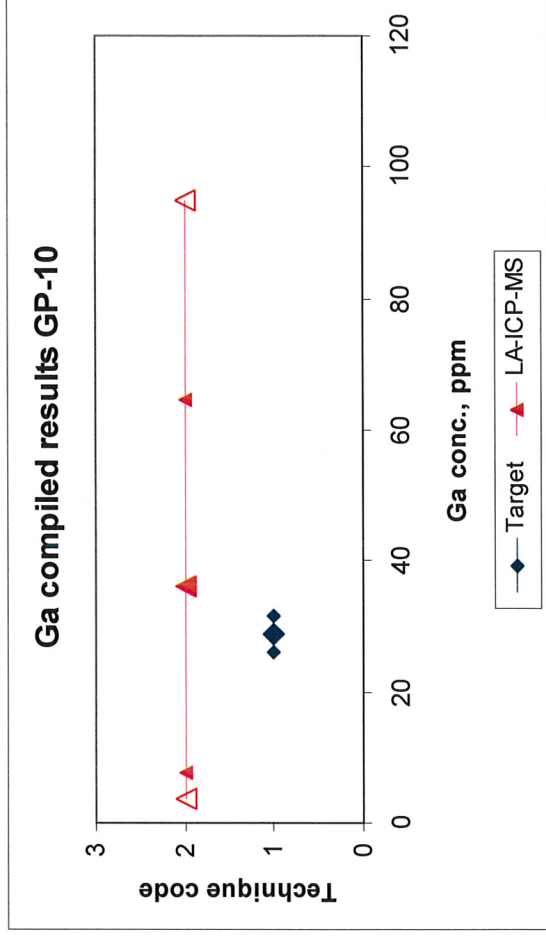


Figure 26. Ga results G-probe 10 study

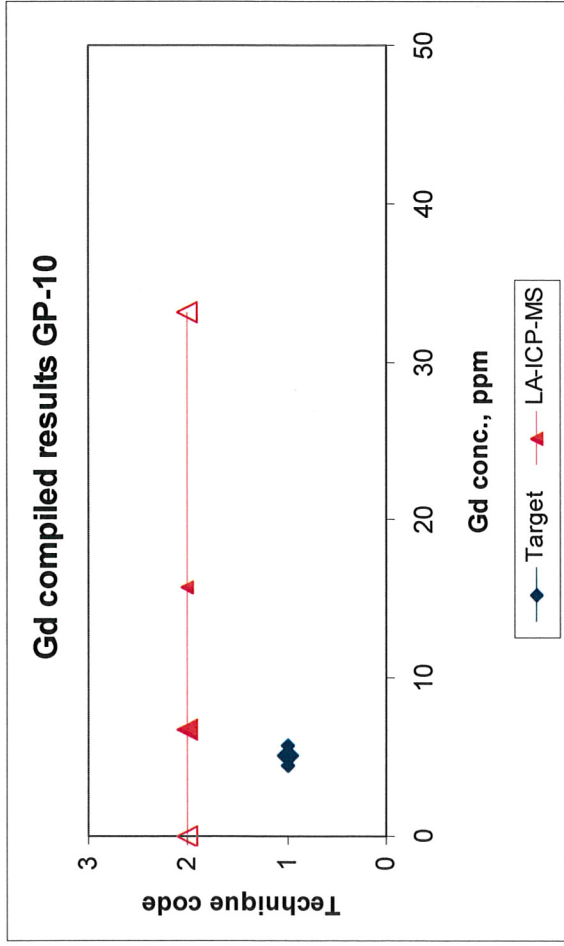


Figure 27. Gd results G-probe 10 study

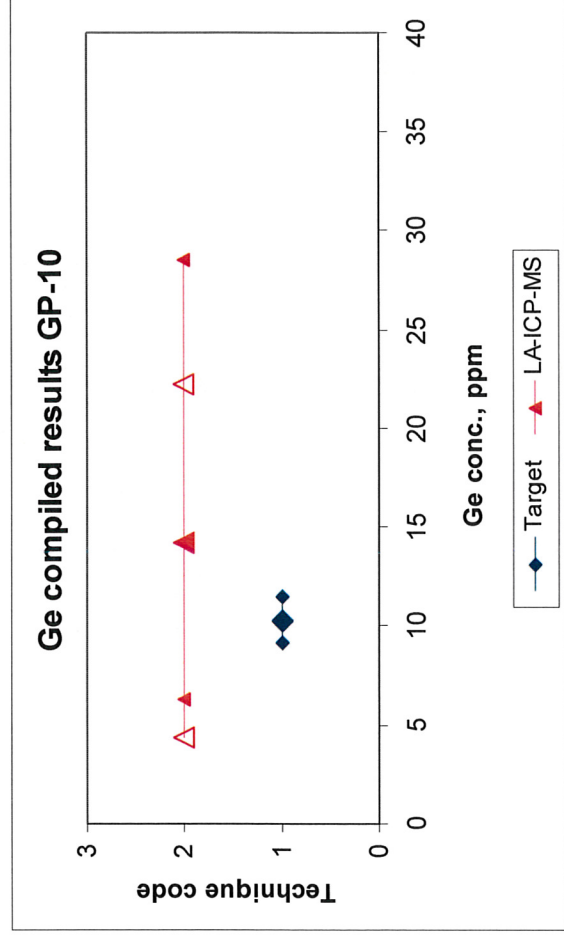


Figure 28. Ge results G-probe 10 study

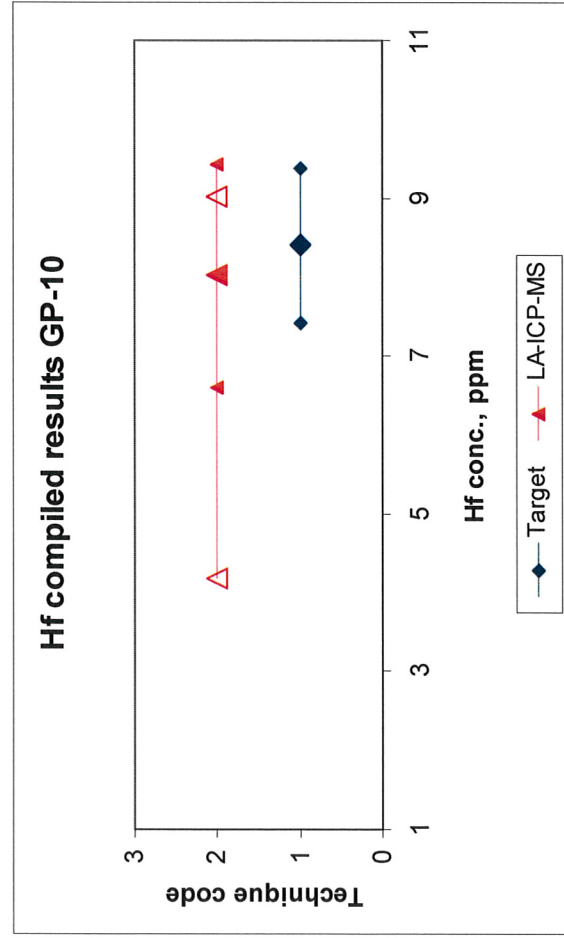


Figure 29. Hf results G-probe 10 study

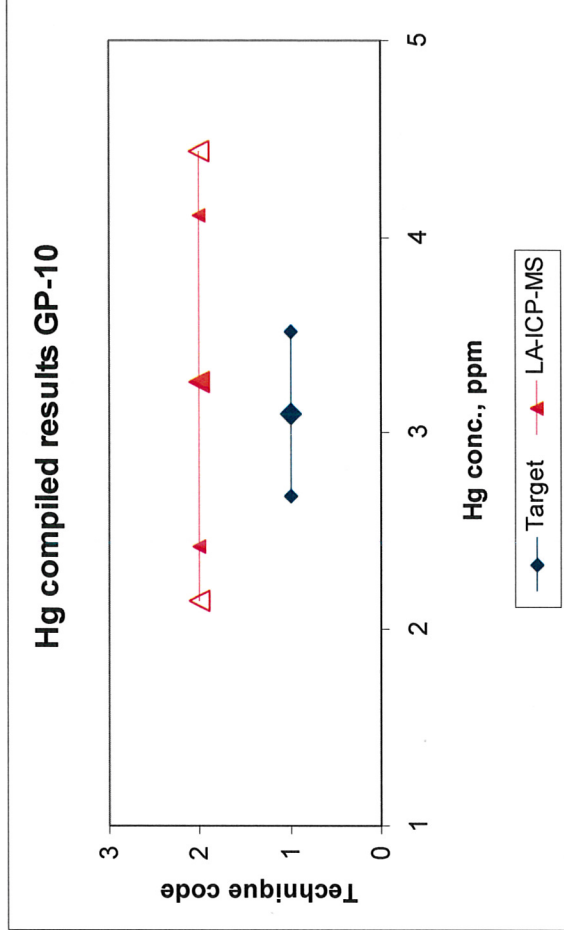


Figure 30. Hg results G-probe 10 study

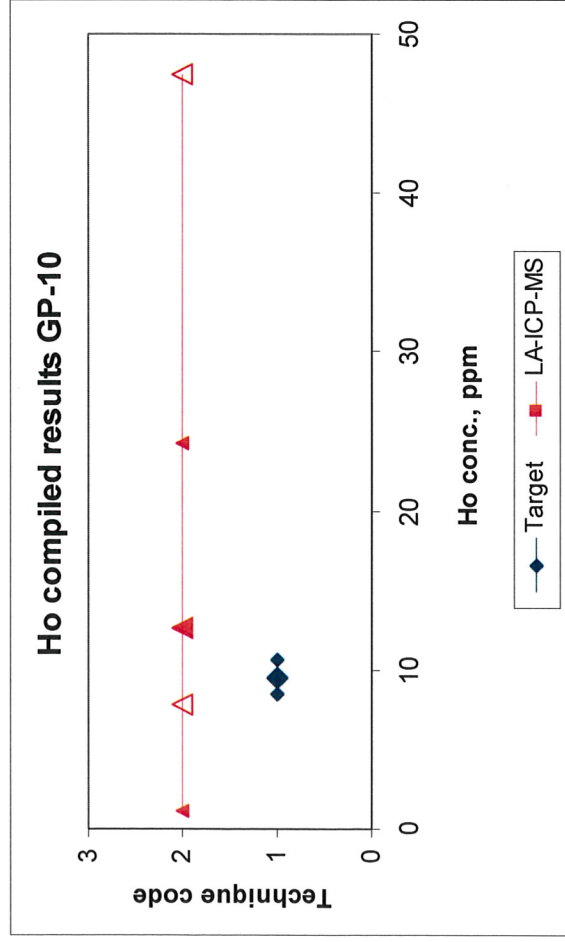


Figure 31 Ho results G-probe 10 study

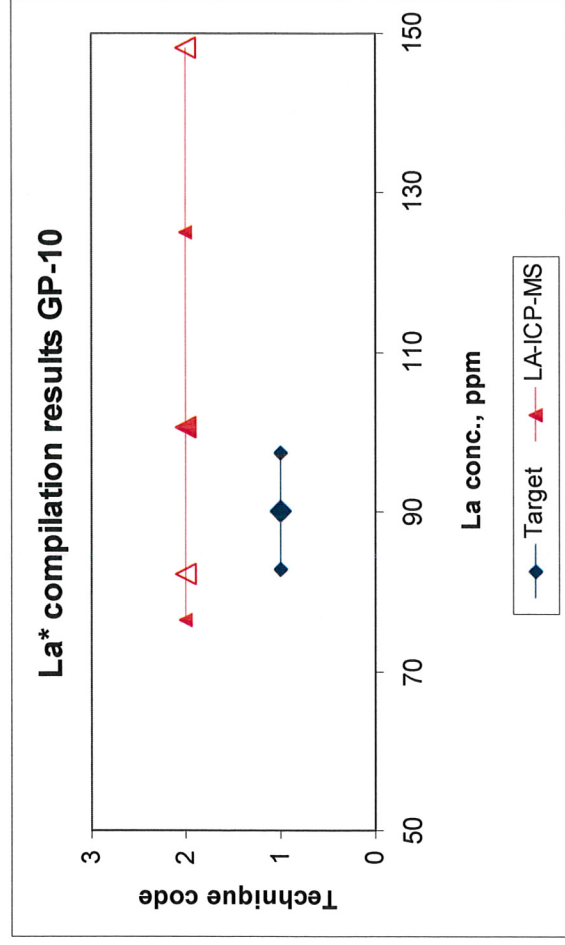


Figure 32. La results G-probe 10 study

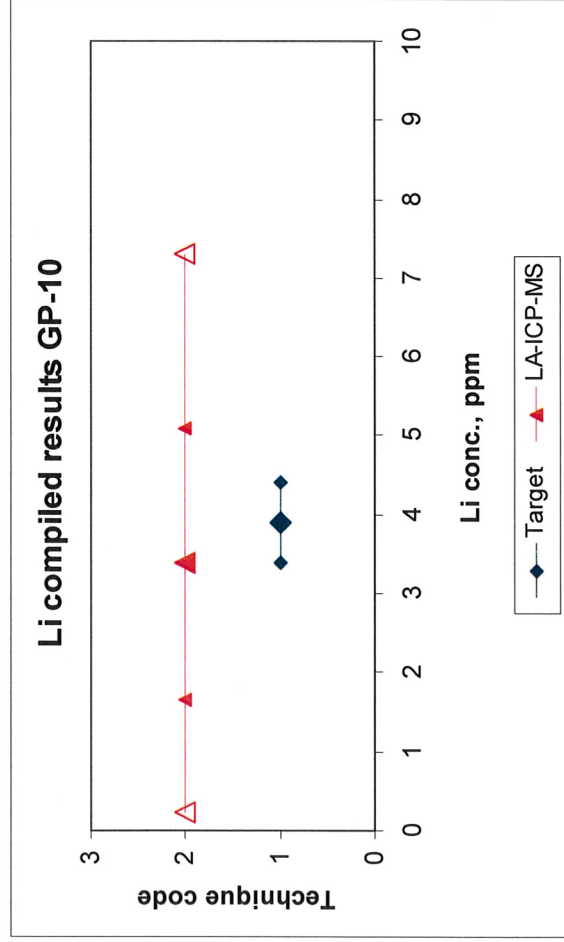


Figure 33 Li results G-probe 10 study

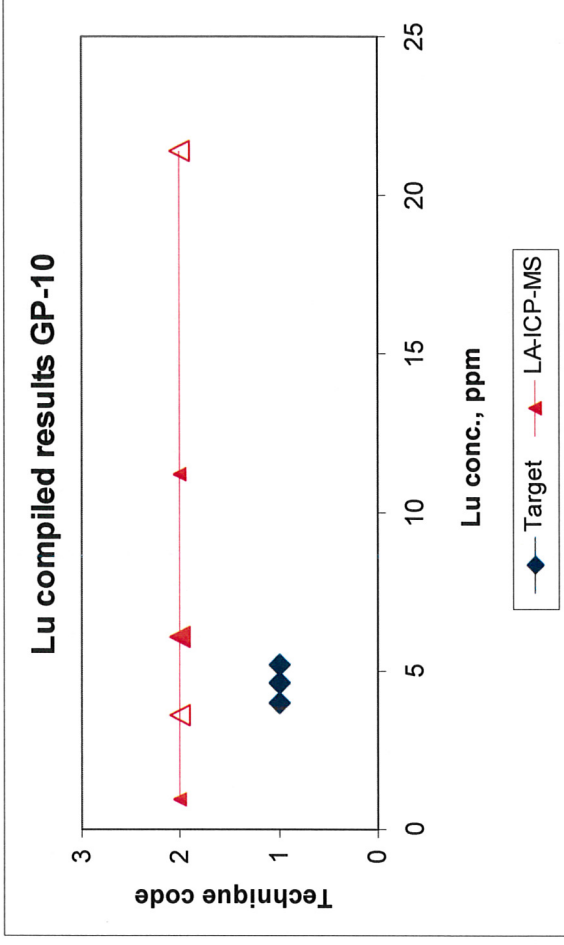


Figure 34 Lu results G-probe 10 study

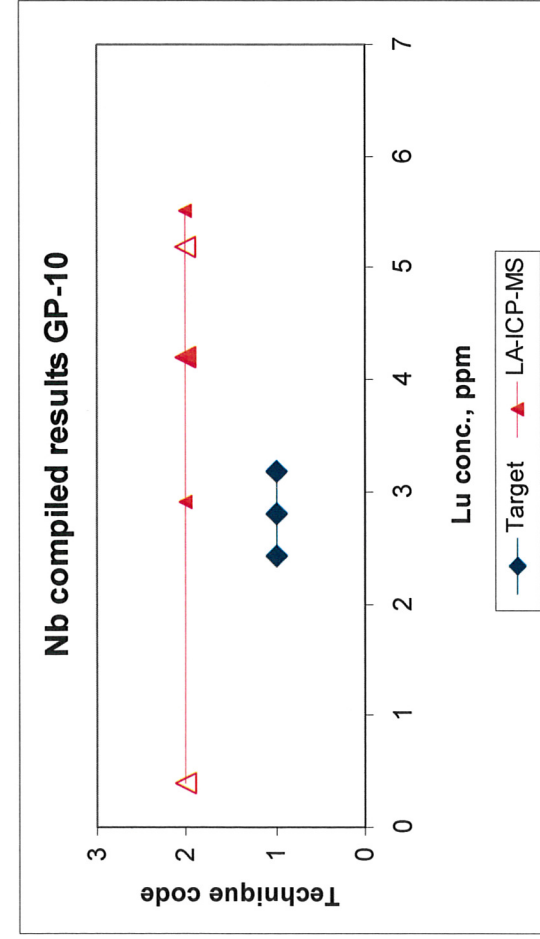


Figure 35. Nb results G-probe 10 study

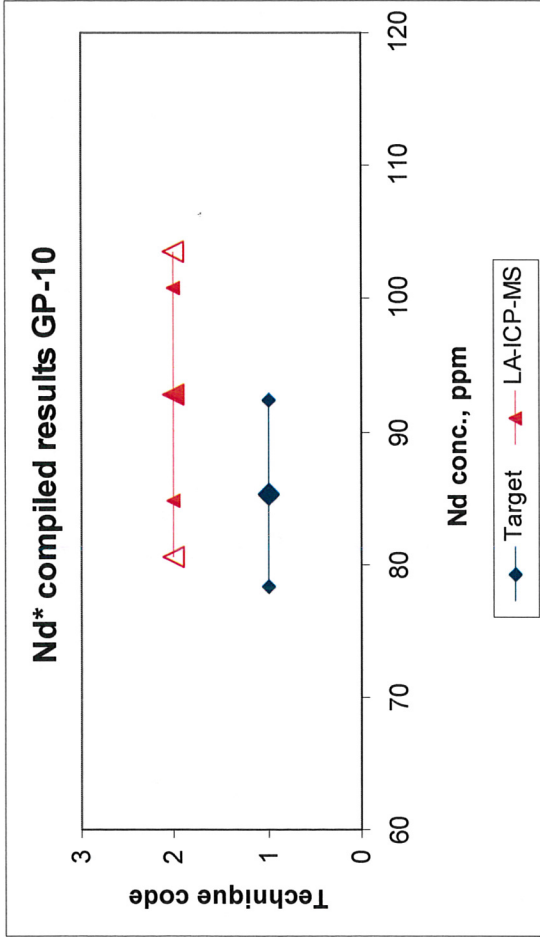


Figure 36. Nd results G-probe 10 study

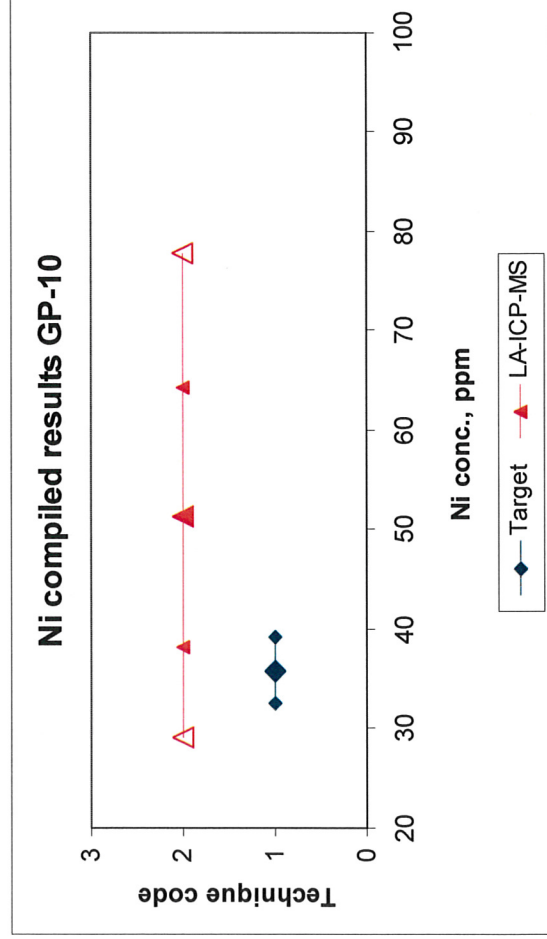


Figure 37. Ni results G-probe 10 study

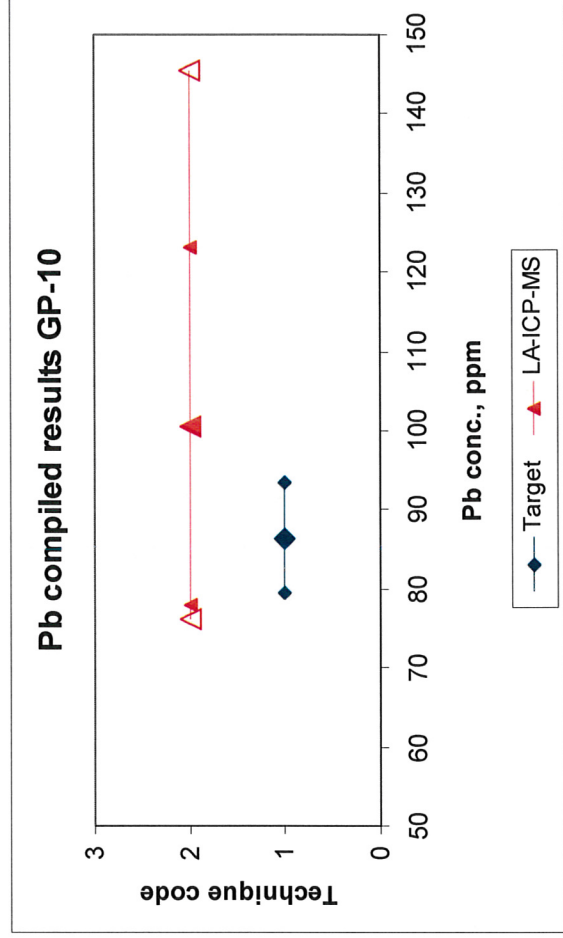


Figure 38 Pb results G-probe 10 study

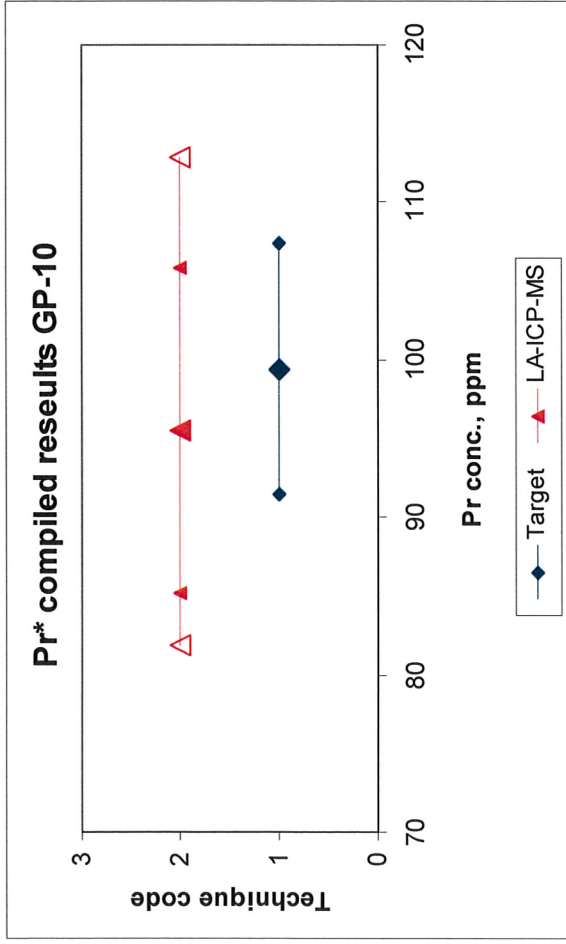


Figure 39. Pr* results G-probe 10 study

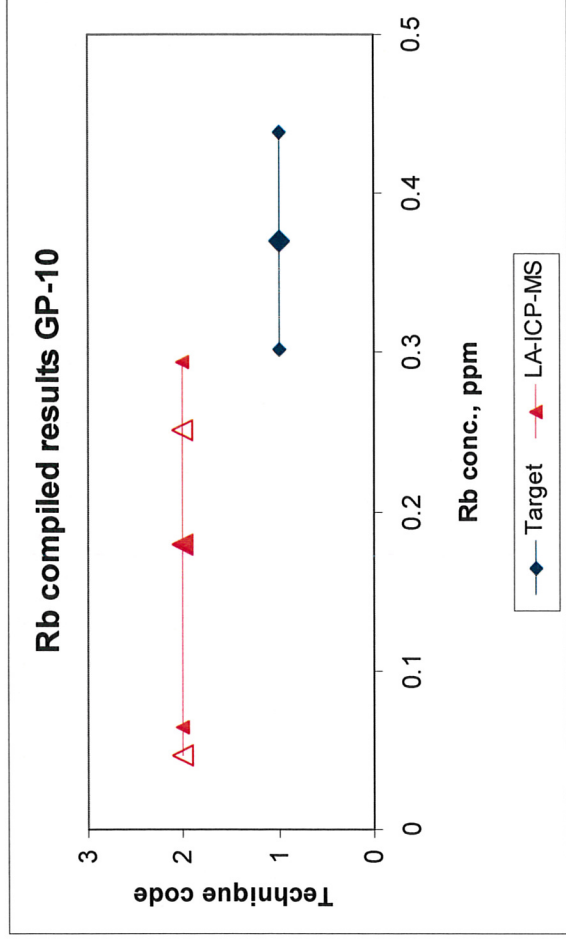


Figure 40. Rb results G-probe 10 study

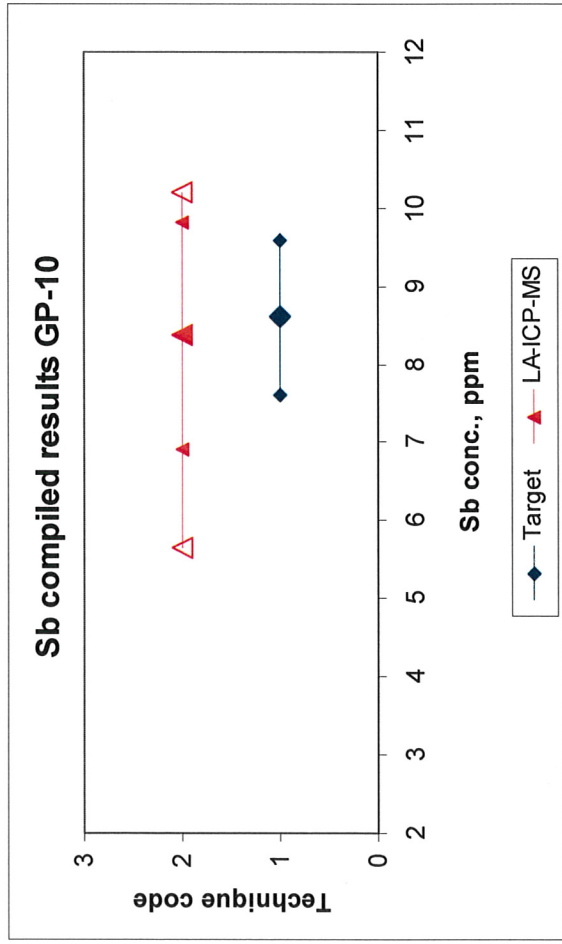


Figure 41. Sb results G-probe 10 study

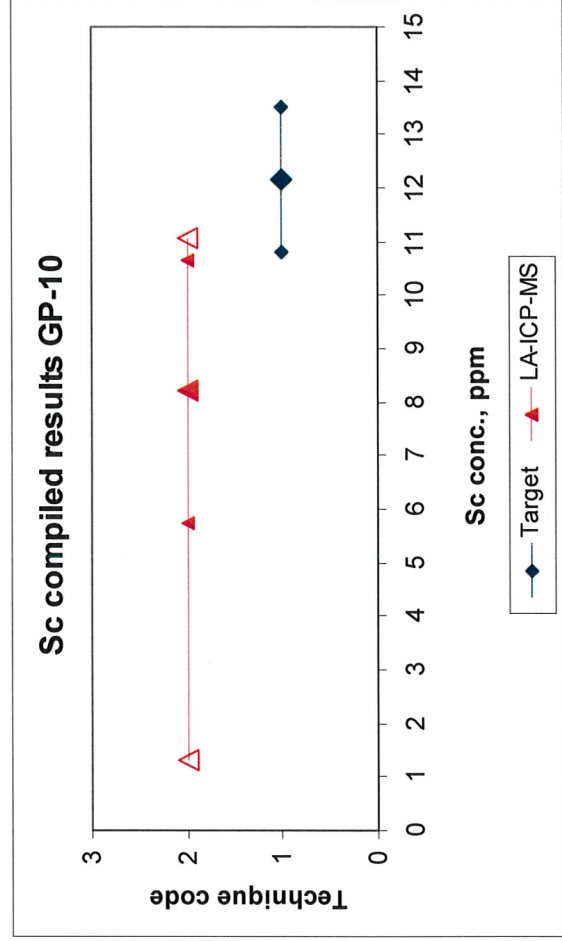


Figure 42. Sc results G-probe 10 study

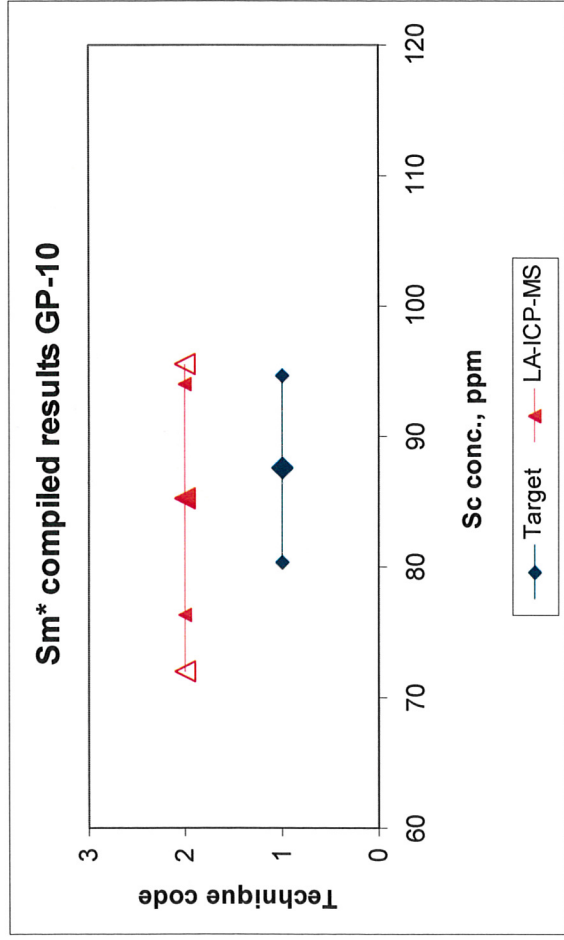


Figure 43. Sm results G-probe 10 study

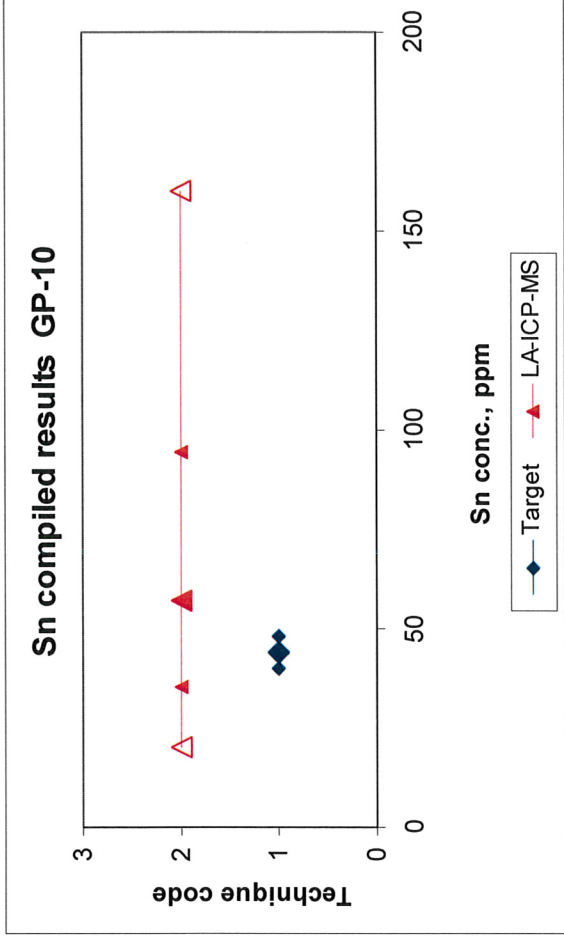


Figure 44. Sn results G-probe 10 study

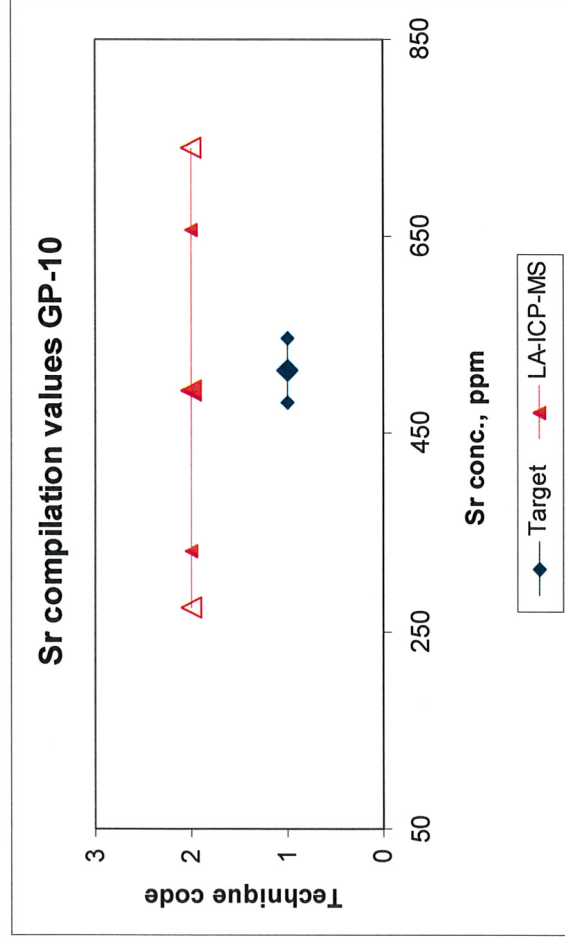


Figure 45. Sr results G-probe 10 study

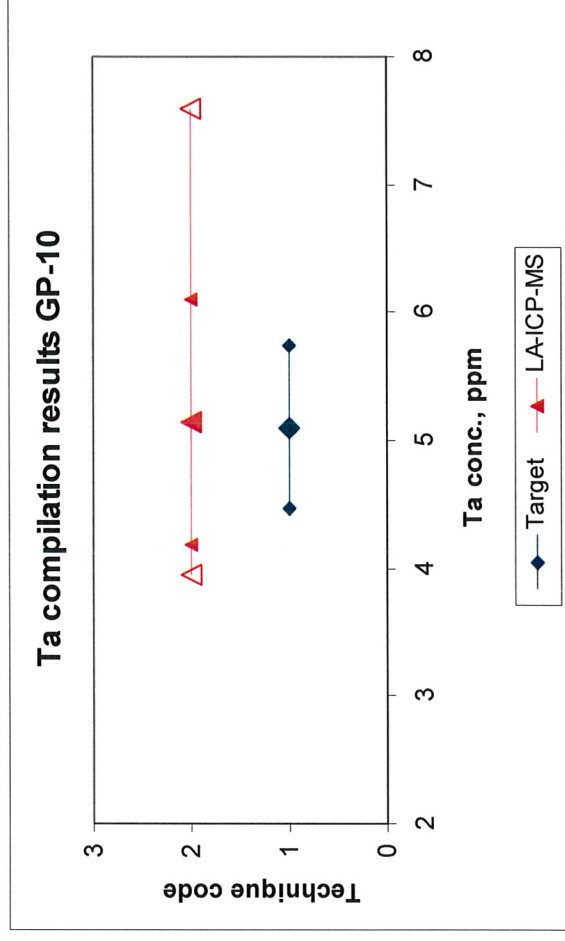


Figure 46. Ta results G-probe 10 study

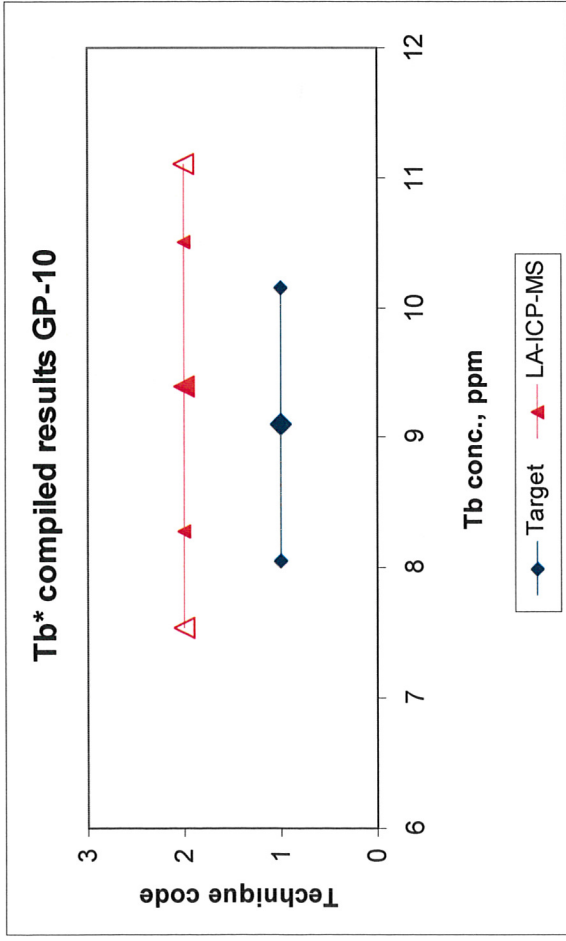


Figure 47. Tb* results G-probe 10 study

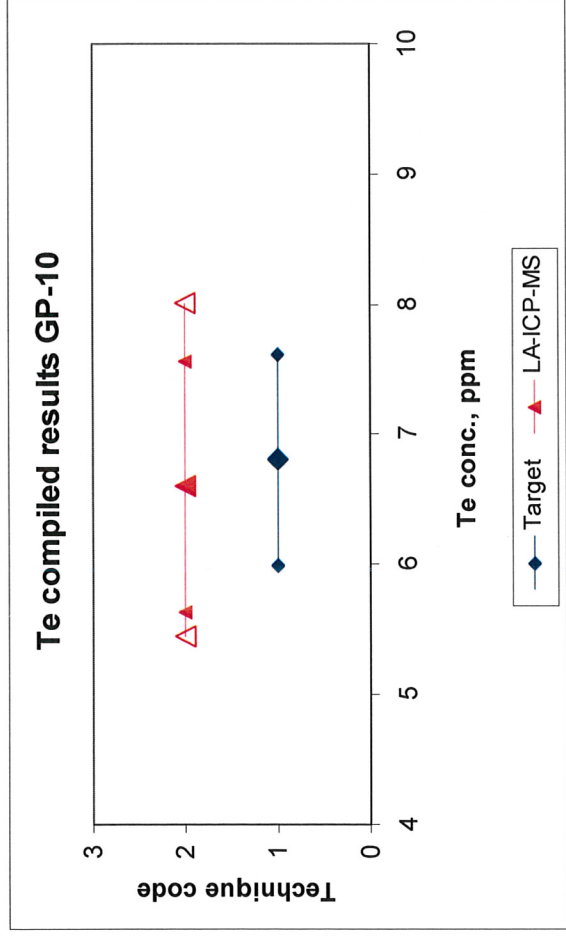


Figure 48. Te results G-probe 10 study

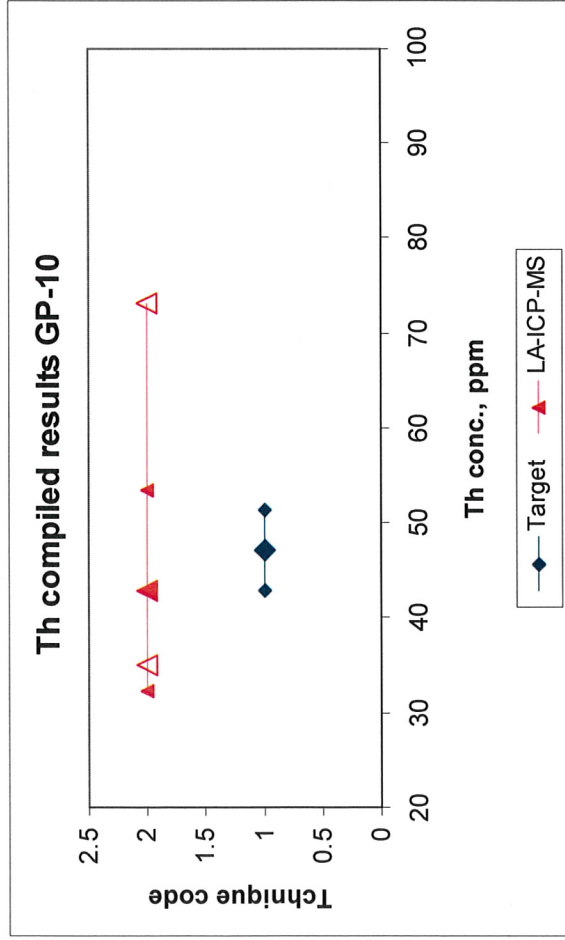


Figure 49. Th results G-probe 10 study

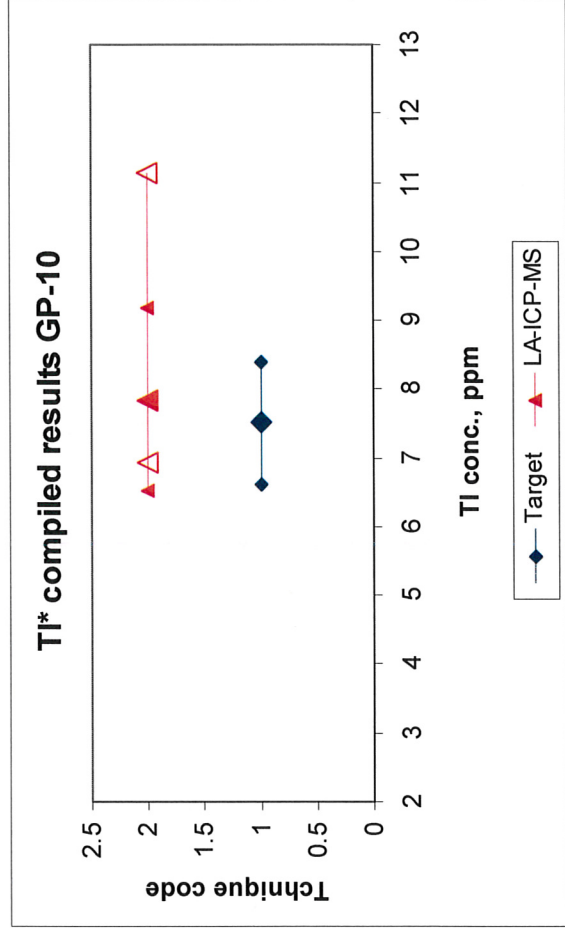


Figure 50. Tl* results G-probe 10 study

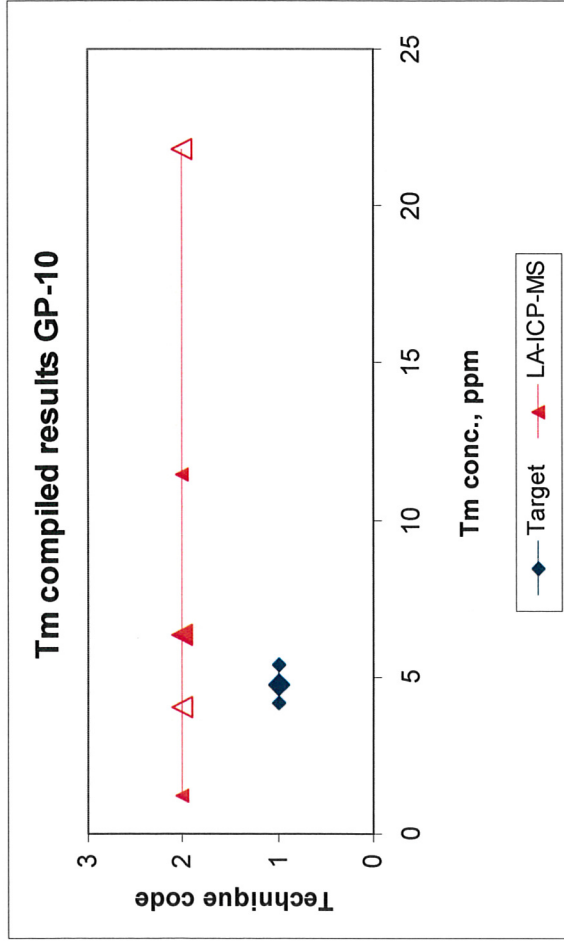


Figure 51. Tm results G-probe 10 study

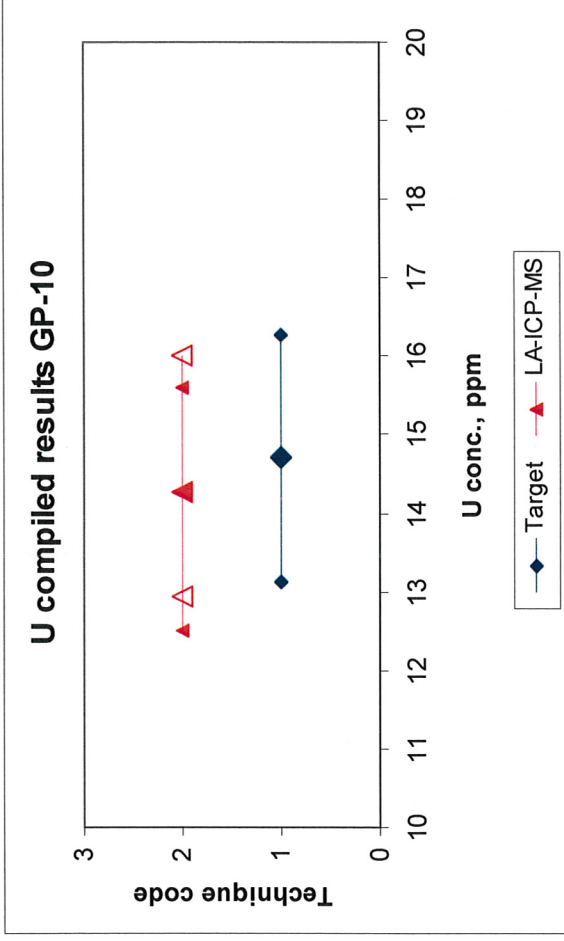


Figure 52. U results G-probe 10 study

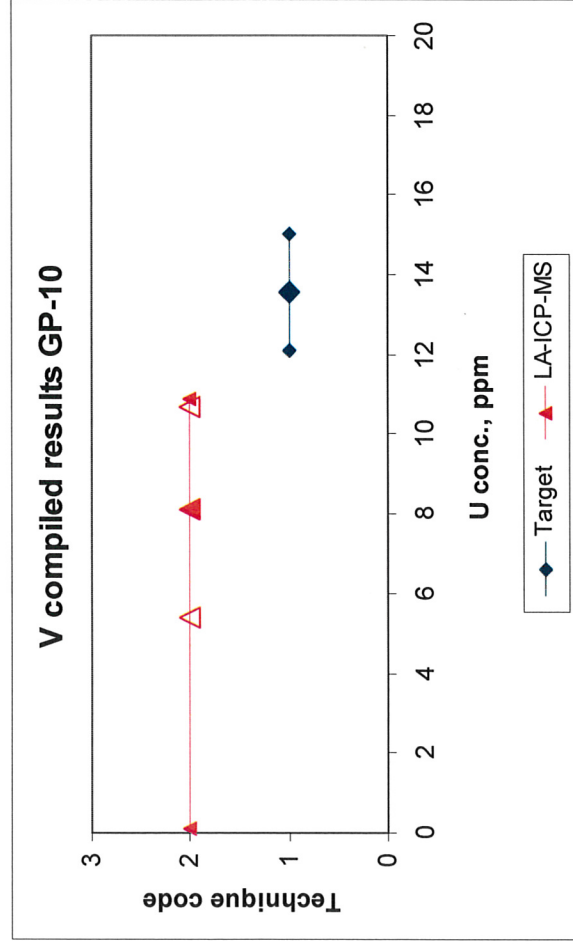


Figure 53. V results G-probe 10 study

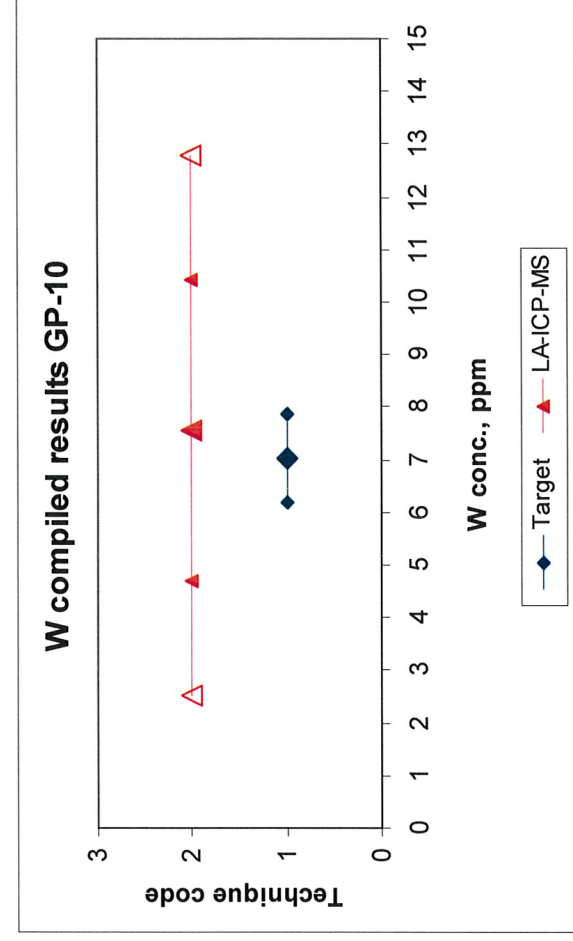


Figure 54. W results G-probe 10 study

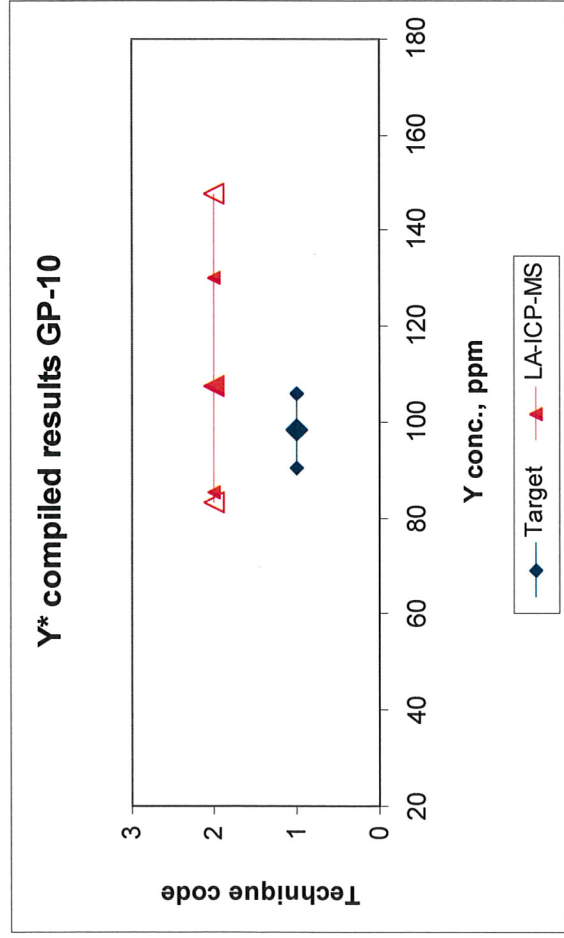


Figure 55. Y* results G-probe 10 study

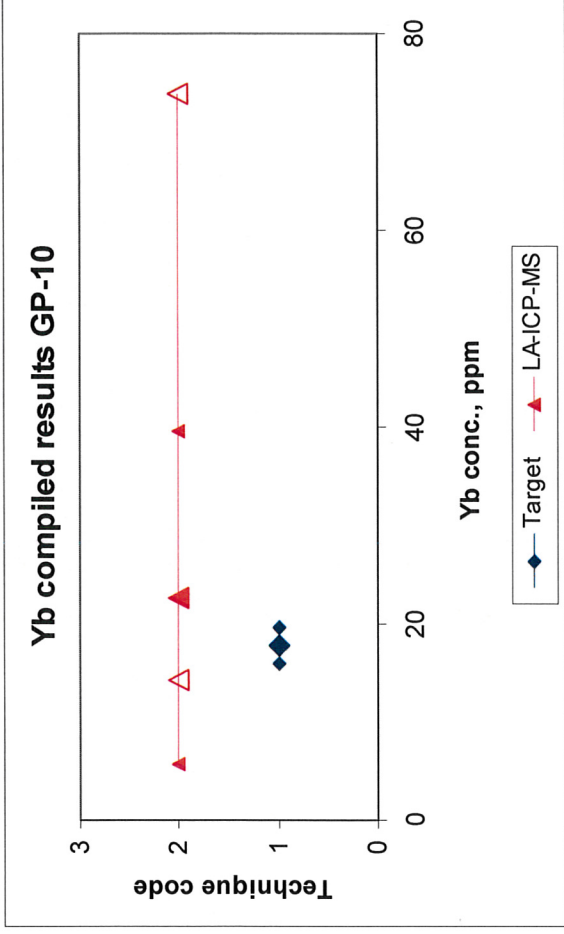


Figure 56. Yb results G-probe 10 study

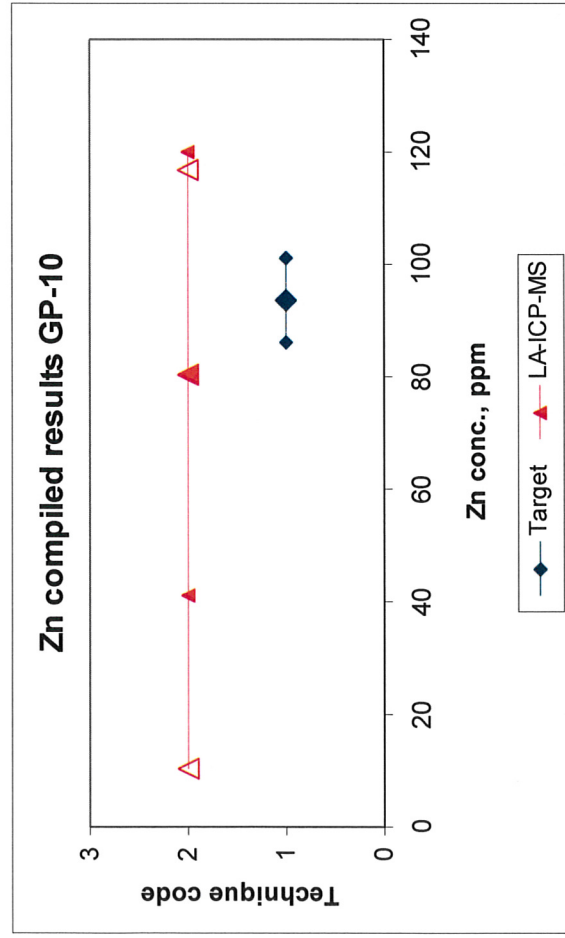


Figure 57. Zn results G-probe 10 study

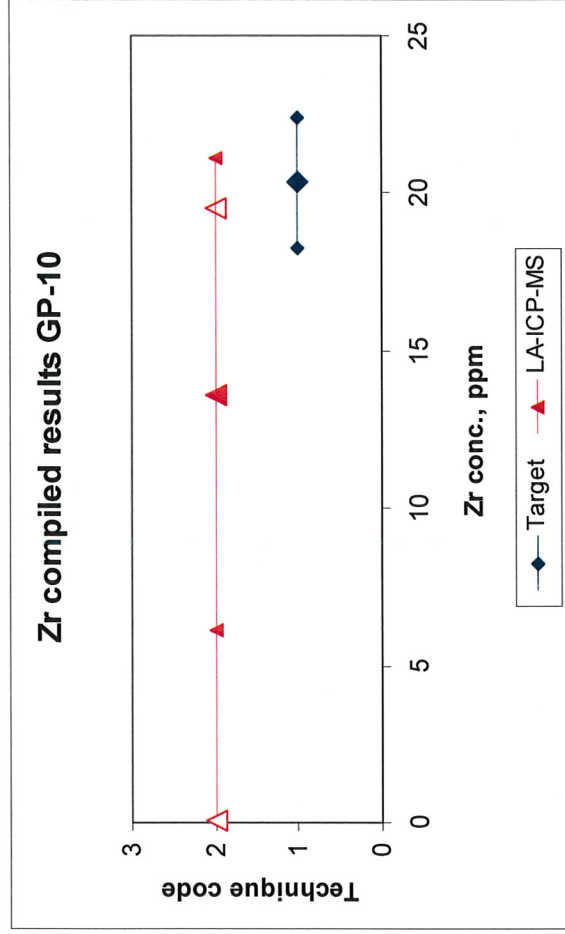


Figure 58. Zr results G-probe 10 study

Table 2. Summary results for GP-10, GP-MAPS

| Oxide | Xa % m/m | Ha % m/m | s.d.m. % m/m | GP-10 AVG. % m/m | Max % m/m | Min % m/m |
|---------|-------------|-------------|-----------------|---------------------|--------------|--------------|
| SiO2 | 3.04 | 0.103 | 0.198 | 0.555 | 0.740 | 0.346 |
| TiO2 | 0.005 | 0.0004 | 0.0659 | 0.054 | 0.127 | 0.006 |
| Al2O3 | 0.49 | 0.022 | 1.573 | 1.124 | 4.360 | 0.340 |
| Fe2O3T | 0.04 | 0.003 | 0.010 | 0.049 | 0.066 | 0.037 |
| Fe(II)O | 0.04 | 0.002 | - | 0.006 | 0.006 | 0.006 |
| MnO | 0.01 | 0.001 | 0.009 | 0.010 | 0.035 | 0.006 |
| MgO | 0.06 | 0.004 | 0.494 | 0.309 | 1.36 | 0.069 |
| CaO | 49.96 | 1.109 | 0.501 | 49.65 | 49.97 | 48.56 |
| Na2O | 0.21 | 0.011 | 0.182 | 0.253 | 0.610 | 0.108 |
| K2O | 0.01 | 0.001 | 0.005 | 0.008 | 0.012 | 0.002 |
| P2O5 | 33.95 | 0.799 | 1.692 | 37.36 | 40.34 | 35.93 |

| Element | Xa % m/m | Ha % m/m | s.d.m. % m/m | GP-10 AVG. % m/m | Max % m/m | Min % m/m |
|---------|-------------|-------------|-----------------|---------------------|--------------|--------------|
| Ag | 2.2 | 0.3 | 2.5 | 2.9 | 10.4 | 1.2 |
| As* | 45.3 | 4.1 | 10.8 | 48.1 | 1116 | 36.2 |
| B | 50.0 | 4.4 | 28.8 | 37.6 | 87.2 | 16.5 |
| Ba | 124.7 | 9.6 | 44.0 | 92.6 | 141.0 | 13.0 |
| Be | 6.8 | 0.8 | 1.7 | 5.7 | 9.1 | 3.1 |
| Bi* | 7.3 | 0.9 | 1.4 | 7.8 | 37.9 | 6.8 |
| Cd | 9.6 | 1.1 | 4.1 | 11.1 | 21.8 | 8.2 |
| Ce* | 100.4 | 8.0 | 25.8 | 90.7 | 374 | 56.5 |
| Co | 44.0 | 4.0 | 10.4 | 43.1 | 55.2 | 15.4 |
| Cr | 29.9 | 2.9 | 21.0 | 32.6 | 79.3 | 17.1 |
| Cs | 0.1 | 0.0 | 0.0 | 0.1 | 0.2 | 0.1 |
| Cu | 100.5 | 8.0 | 21.0 | 94.4 | 138 | 61.6 |
| Dy* | 47.5 | 4.2 | 5.3 | 46.9 | 265 | 38.6 |
| Er* | 20.3 | 2.1 | 2.5 | 19.2 | 123 | 15.6 |
| Eu | 9.1 | 1.0 | 2.9 | 9.6 | 18.1 | 7.4 |
| Ga | 28.8 | 2.8 | 32.3 | 37.2 | 95.0 | 3.7 |
| Gd | 5.1 | 0.6 | 9.0 | 6.7 | 33.1 | 0.0 |
| Ge | 10.3 | 1.2 | 8.0 | 14.2 | 28.5 | 4.4 |
| Hf | 8.4 | 1.0 | 1.4 | 8.0 | 9.0 | 4.2 |

| Element | Xa % m/m | Ha % m/m | s.d.m. % m/m | GP-10 AVG. % m/m | Max % m/m | Min % m/m |
|---------|-------------|-------------|-----------------|---------------------|--------------|--------------|
| Hg | 3.1 | 0.4 | - | - | - | - |
| Ho | 9.5 | 1.1 | 11.6 | 12.7 | 47.5 | 7.8 |
| In | 19.5 | 2.0 | 3.1 | 19.5 | 23.4 | 16.7 |
| La* | 90.0 | 7.3 | 24.3 | 100.7 | 246 | 82.2 |
| Li | 3.9 | 0.5 | 1.7 | 3.4 | 7.3 | 0.2 |
| Lu | 4.6 | 0.6 | 5.1 | 6.1 | 21.4 | 3.6 |
| Mo | 1.6 | 0.2 | - | - | - | - |
| Nb | 2.8 | 0.4 | 1.3 | 4.2 | 5.2 | 0.4 |
| Nd* | 85.3 | 7.0 | 8.0 | 92.8 | 590 | 80.5 |
| Ni | 35.8 | 3.3 | 13.0 | 51.3 | 77.8 | 29.0 |
| Pb | 86.4 | 7.1 | 22.6 | 101 | 145 | 76.2 |
| Pr* | 99.4 | 8.0 | 10.3 | 95.5 | 351 | 81.9 |
| Rb | 0.4 | 0.1 | 0.1 | 0.2 | 0.3 | 0.0 |
| Sb | 8.6 | 1.0 | 1.4 | 8.4 | 10.2 | 5.6 |
| Sc | 12.2 | 1.3 | 2.5 | 8.2 | 11.1 | 1.3 |
| Se | 9.2 | 7.1 | 0.9 | 9.2 | 9.8 | 8.5 |
| Sm* | 87.5 | 4.0 | 8.8 | 85.2 | 641 | 72.0 |
| Sn | 43.9 | 4.0 | 37.0 | 57.2 | 160 | 35.1 |
| Sr | 514 | 32 | 163 | 494 | 740 | 273 |
| Ta | 5.1 | 0.6 | 1.0 | 5.1 | 7.6 | 4.0 |
| Tb* | 9.1 | 1.0 | 1.1 | 9.4 | 62.9 | 7.5 |
| Te | 6.8 | 0.8 | 1.0 | 6.6 | 8.0 | 5.4 |
| Th | 47.2 | 4.2 | 10.6 | 42.8 | 73.1 | 35.1 |
| Tl* | 7.5 | 0.9 | 1.3 | 7.8 | 52.3 | 6.9 |
| Tm | 4.8 | 0.6 | 5.1 | 6.3 | 21.8 | 4.0 |
| U | 14.7 | 1.6 | 1.3 | 14.3 | 16.0 | 12.5 |
| V | 13.6 | 1.5 | 2.7 | 8.1 | 10.7 | 0.1 |
| W | 7.0 | 0.8 | 2.8 | 7.6 | 12.8 | 2.5 |
| Y* | 98.2 | 7.9 | 22.5 | 108 | 566 | 83.1 |
| Yb | 17.7 | 1.8 | 17.0 | 22.7 | 73.8 | 14.3 |
| Zn | 93.5 | 7.6 | 39.4 | 80.5 | 116.9 | 10.5 |
| Zr | 20.3 | 2.1 | 7.5 | 13.6 | 19.5 | 0.1 |

Xa Target value obtained from USGS bulk analysis
Ha Target precision calculated using modified version of Horowitz equation
X* Element mean concentration and standard deviation determined from outlier rejected data set.
s.d.m. Standard deviation of population mean
mean Mean element concentration for all techniques reporting
Max. Maximum element/oxide concentration all labs reporting
Min. Minimum element/oxide concentration all labs reporting