

## Analytical Methods

### Electronic Supplementary Information File

#### **Attenuation of interferences in collision/reaction cell inductively coupled plasma mass spectrometry, using helium and hydrogen as cell gases – Application to multi-element analysis of mastic gum**

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## Supplementary File

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**Table S1** Isotopes of interest and potentially polyatomic interferences  
(non-restrictive list)

Isotope	Potentially interfering species
<sup>24</sup> Mg	<sup>12</sup> C <sub>2</sub> <sup>+</sup>
<sup>27</sup> Al	<sup>11</sup> B <sup>16</sup> O <sup>+</sup> , <sup>12</sup> C <sub>2</sub> <sup>1</sup> H <sub>3</sub> <sup>+</sup> , <sup>1</sup> H <sup>12</sup> C <sup>14</sup> N <sup>+</sup> , <sup>12</sup> C <sup>15</sup> N <sup>+</sup> , <sup>13</sup> C <sup>14</sup> N <sup>+</sup>
<sup>39</sup> K	<sup>38</sup> Ar <sup>1</sup> H <sup>+</sup>
<sup>42</sup> Ca	<sup>14</sup> N <sub>3</sub> <sup>+</sup> , <sup>26</sup> Mg <sup>16</sup> O <sup>+</sup> , <sup>40</sup> Ar <sup>1</sup> H <sub>2</sub> <sup>+</sup>
<sup>43</sup> Ca	<sup>14</sup> N <sub>3</sub> <sup>1</sup> H <sup>+</sup> , <sup>27</sup> Al <sup>16</sup> O <sup>+</sup>
<sup>47</sup> Ti	<sup>32</sup> S <sup>14</sup> N <sup>1</sup> H <sup>+</sup> , <sup>12</sup> C <sup>35</sup> Cl <sup>+</sup> , <sup>31</sup> P <sup>16</sup> O <sup>+</sup> , <sup>15</sup> N <sup>16</sup> O <sub>2</sub> <sup>+</sup> , <sup>33</sup> S <sup>14</sup> N <sup>+</sup> , <sup>30</sup> Si <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>32</sup> S <sup>15</sup> N <sup>+</sup>
<sup>51</sup> V	<sup>35</sup> Cl <sup>16</sup> O <sup>+</sup> , <sup>37</sup> Cl <sup>14</sup> N <sup>+</sup> , <sup>40</sup> Ar <sup>11</sup> B <sup>+</sup> , <sup>34</sup> S <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>36</sup> Ar <sup>15</sup> N <sup>+</sup> , <sup>36</sup> Ar <sup>14</sup> N <sup>1</sup> H <sup>+</sup> , <sup>38</sup> Ar <sup>13</sup> C <sup>+</sup> , <sup>36</sup> S <sup>15</sup> N <sup>+</sup> , <sup>33</sup> S <sup>18</sup> O <sup>+</sup> , <sup>34</sup> S <sup>17</sup> O <sup>+</sup>
<sup>52</sup> Cr	<sup>36</sup> Ar <sup>16</sup> O <sup>+</sup> , <sup>40</sup> Ar <sup>12</sup> C <sup>+</sup> , <sup>35</sup> Cl <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>37</sup> Cl <sup>14</sup> N <sup>1</sup> H <sup>+</sup> , <sup>34</sup> S <sup>18</sup> O <sup>+</sup> , <sup>38</sup> Ar <sup>14</sup> N <sup>+</sup> , <sup>37</sup> Cl <sup>15</sup> N <sup>+</sup> , <sup>36</sup> S <sup>16</sup> O <sup>+</sup> , <sup>36</sup> Ar <sup>15</sup> N <sup>1</sup> H <sup>+</sup> , <sup>35</sup> Cl <sup>17</sup> O <sup>+</sup>
<sup>53</sup> Cr	<sup>36</sup> Ar <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>40</sup> Ar <sup>13</sup> C <sup>+</sup> , <sup>37</sup> Cl <sup>16</sup> O <sup>+</sup> , <sup>35</sup> Cl <sup>18</sup> O <sup>+</sup> , <sup>40</sup> Ar <sup>12</sup> C <sup>1</sup> H <sup>+</sup> , <sup>38</sup> Ar <sup>15</sup> N <sup>+</sup> , <sup>38</sup> Ar <sup>14</sup> N <sup>1</sup> H <sup>+</sup> , <sup>36</sup> Ar <sup>17</sup> O <sup>+</sup>
<sup>55</sup> Mn	<sup>40</sup> Ar <sup>14</sup> N <sup>1</sup> H <sup>+</sup> , <sup>40</sup> Ar <sup>15</sup> N <sup>+</sup> , <sup>39</sup> K <sup>16</sup> O <sup>+</sup> , <sup>23</sup> Na <sup>32</sup> S <sup>+</sup> , <sup>37</sup> Cl <sup>18</sup> O <sup>+</sup> , <sup>38</sup> Ar <sup>17</sup> O <sup>+</sup> , <sup>36</sup> Ar <sup>18</sup> O <sup>1</sup> H <sup>+</sup> , <sup>38</sup> Ar <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>37</sup> Cl <sup>17</sup> O <sup>1</sup> H <sup>+</sup>
<sup>56</sup> Fe	<sup>40</sup> Ar <sup>16</sup> O <sup>+</sup> , <sup>40</sup> Ca <sup>16</sup> O <sup>+</sup> , <sup>40</sup> Ar <sup>15</sup> O <sup>1</sup> H <sup>+</sup> , <sup>38</sup> Ar <sup>18</sup> O <sup>+</sup> , <sup>38</sup> Ar <sup>17</sup> O <sup>1</sup> H <sup>+</sup> , <sup>23</sup> Na <sup>16</sup> O <sub>2</sub> <sup>1</sup> H <sup>+</sup> , <sup>24</sup> Mg <sup>16</sup> O <sub>2</sub> <sup>+</sup> , <sup>40</sup> Ar <sup>15</sup> N <sup>1</sup> H <sup>+</sup> , <sup>37</sup> Cl <sup>18</sup> O <sup>1</sup> H <sup>+</sup>
<sup>57</sup> Fe	<sup>40</sup> Ar <sup>17</sup> O <sup>+</sup> , <sup>40</sup> Ar <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>38</sup> Ar <sup>18</sup> O <sup>1</sup> H <sup>+</sup> , <sup>40</sup> Ca <sup>16</sup> O <sup>1</sup> H <sup>+</sup>
<sup>59</sup> Co	<sup>36</sup> Ar <sup>23</sup> Na <sup>+</sup> , <sup>24</sup> Mg <sup>35</sup> Cl <sup>+</sup> , <sup>42</sup> Ca <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>23</sup> Na <sup>35</sup> Cl <sup>1</sup> H <sup>+</sup> , <sup>43</sup> Ca <sup>16</sup> O <sup>+</sup> , <sup>40</sup> Ar <sup>18</sup> O <sup>1</sup> H <sup>+</sup> , <sup>58</sup> Ni <sup>1</sup> H <sup>+</sup>
<sup>60</sup> Ni	<sup>23</sup> Na <sup>37</sup> Cl <sup>+</sup> , <sup>25</sup> Mg <sup>35</sup> Cl <sup>+</sup> , <sup>43</sup> Ca <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>44</sup> Ca <sup>16</sup> O <sup>+</sup> , <sup>59</sup> Co <sup>1</sup> H <sup>+</sup> , <sup>36</sup> Ar <sup>24</sup> Mg <sup>+</sup>
<sup>63</sup> Cu	<sup>40</sup> Ar <sup>23</sup> Na <sup>+</sup> , <sup>40</sup> Ca <sup>23</sup> Na <sup>+</sup> , <sup>12</sup> C <sup>16</sup> O <sup>35</sup> Cl <sup>+</sup> , <sup>12</sup> C <sup>14</sup> N <sup>37</sup> Cl <sup>+</sup> , <sup>31</sup> P <sup>16</sup> O <sub>2</sub> <sup>+</sup> , <sup>47</sup> Ti <sup>16</sup> O <sup>+</sup> , <sup>46</sup> Ca <sup>16</sup> O <sup>1</sup> H <sup>+</sup>
<sup>65</sup> Cu	<sup>40</sup> Ar <sup>25</sup> Mg <sup>+</sup> , <sup>40</sup> Ar <sup>24</sup> Mg <sup>1</sup> H <sup>+</sup> , <sup>32</sup> S <sup>16</sup> O <sub>2</sub> <sup>1</sup> H <sup>+</sup> , <sup>32</sup> S <sub>2</sub> <sup>1</sup> H <sup>+</sup> , <sup>33</sup> S <sup>16</sup> O <sub>2</sub> <sup>+</sup> , <sup>32</sup> S <sup>33</sup> S <sup>+</sup> , <sup>48</sup> Ca <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>49</sup> Ti <sup>16</sup> O <sup>+</sup> , <sup>12</sup> C <sup>16</sup> O <sup>37</sup> Cl <sup>+</sup> , <sup>12</sup> C <sup>18</sup> O <sup>35</sup> Cl <sup>+</sup>
<sup>66</sup> Zn	<sup>40</sup> Ar <sup>26</sup> Mg <sup>+</sup> , <sup>32</sup> S <sup>34</sup> S <sup>+</sup> , <sup>32</sup> S <sup>16</sup> O <sup>18</sup> O <sup>+</sup> , <sup>34</sup> S <sup>16</sup> O <sub>2</sub> <sup>+</sup> , <sup>33</sup> S <sub>2</sub> <sup>+</sup> , <sup>50</sup> Cr <sup>16</sup> O <sup>+</sup> , <sup>50</sup> Ti <sup>16</sup> O <sup>+</sup> , <sup>32</sup> S <sup>34</sup> S <sup>+</sup> , <sup>31</sup> P <sup>18</sup> O <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>32</sup> S <sup>17</sup> O <sub>2</sub> <sup>+</sup> , <sup>33</sup> S <sup>16</sup> O <sup>17</sup> O <sup>+</sup>
<sup>75</sup> As	<sup>40</sup> Ar <sup>35</sup> Cl <sup>+</sup> , <sup>40</sup> Ca <sup>35</sup> Cl <sup>+</sup> , <sup>40</sup> Ar <sup>34</sup> S <sup>1</sup> H <sup>+</sup> , <sup>36</sup> Ar <sup>38</sup> Ar <sup>1</sup> H <sup>+</sup> , <sup>74</sup> Ge <sup>1</sup> H <sup>+</sup> , <sup>43</sup> Ca <sup>16</sup> O <sub>2</sub> <sup>+</sup> , <sup>56</sup> Fe <sup>18</sup> O <sup>1</sup> H <sup>+</sup> , <sup>59</sup> Co <sup>16</sup> O <sup>+</sup> , <sup>58</sup> Ni <sup>16</sup> O <sup>1</sup> H <sup>+</sup> , <sup>23</sup> Na <sup>12</sup> C <sup>40</sup> Ar <sup>+</sup> , <sup>36</sup> Ar <sup>39</sup> K <sup>+</sup> , <sup>38</sup> Ar <sup>37</sup> Cl <sup>+</sup>
<sup>78</sup> Se	<sup>40</sup> Ar <sup>38</sup> Ar <sup>+</sup> , <sup>40</sup> Ar <sup>37</sup> Cl <sup>1</sup> H <sup>+</sup> , <sup>38</sup> Ar <sup>40</sup> Ca <sup>+</sup>
<sup>80</sup> Se	<sup>40</sup> Ar <sup>40</sup> Ar <sup>+</sup> , <sup>40</sup> Ar <sup>40</sup> Ca <sup>+</sup> , <sup>32</sup> S <sup>16</sup> O <sub>3</sub> <sup>+</sup> , <sup>79</sup> Br <sup>1</sup> H <sup>+</sup> , <sup>64</sup> Zn <sup>16</sup> O <sup>+</sup> , <sup>32</sup> S <sub>2</sub> <sup>16</sup> O <sup>+</sup>
<sup>88</sup> Sr	<sup>40</sup> Ar <sup>48</sup> Ca <sup>+</sup> , <sup>38</sup> Ar <sup>50</sup> Ti <sup>+</sup> , <sup>40</sup> Ar <sup>48</sup> Ti <sup>+</sup> , <sup>38</sup> Ar <sup>50</sup> V <sup>+</sup> , <sup>38</sup> Ar <sup>50</sup> Cr <sup>+</sup> , <sup>40</sup> Ca <sup>48</sup> Ca <sup>+</sup> , <sup>70</sup> Zn <sup>18</sup> O <sup>+</sup> , <sup>71</sup> Ga <sup>17</sup> O <sup>+</sup> , <sup>70</sup> Ge <sup>18</sup> O <sup>+</sup> , <sup>72</sup> Ge <sup>16</sup> O <sup>+</sup>
<sup>93</sup> Nb	<sup>77</sup> Se <sup>16</sup> O <sup>+</sup>
<sup>95</sup> Mo	<sup>79</sup> Br <sup>16</sup> O <sup>+</sup> , <sup>40</sup> Ar <sup>39</sup> K <sup>16</sup> O <sup>+</sup> , <sup>40</sup> Ar <sup>38</sup> Ar <sup>17</sup> O <sup>+</sup>
<sup>107</sup> Ag	<sup>91</sup> Zr <sup>16</sup> O <sup>+</sup>
<sup>111</sup> Cd	<sup>79</sup> Br <sup>32</sup> S <sup>+</sup> , <sup>95</sup> Mo <sup>16</sup> O <sup>+</sup> , <sup>94</sup> Zr <sup>16</sup> O <sup>1</sup> H <sup>+</sup>
<sup>137</sup> Ba	<sup>121</sup> Sb <sup>16</sup> O <sup>+</sup>

## **Introduction**

For complicated matrices, like resins and gums, there is decomposition difficulties,<sup>1</sup> so sample preparation is a critical step for the elemental analysis. The correlation of factorial design and microwave assisted acid digestion helps to accelerate the sample pretreatment step and improves the accuracy of results.<sup>2</sup> The factors that are usually optimized during the process of digestion with microwave oven are the power, the pressure and the temperature of the oven, the time of digestion, the sample mass (imposed response correction to the individual mass), the volume of each reagent (acid) or the total volume or even the ratio of volumes of specific reagents.<sup>2-9</sup>

## **Sample digestion procedure**

Initially, different experiments were performed in order to find the most suitable sample mass that will be used for the further experiments. Mastic sample masses ranged from 0.1 g to 0.5 g were digested at different temperatures and acids volumes. The results showed that the mastic samples were not completely dissolved when 0.5 g was used, even if the maximum temperature (230° C) was applied in conjunction with the larger volume of the acids (10 mL). Similar results were achieved when the applied temperature ranged from 150° C to 180° C. Furthermore, some of the samples with masses ranged from 0.3 to 0.4 g left residuals into the vessels even when the digestion held at high temperatures with a large volume of acids, so these masses considered as non-optimal. Finally, a mass of 0.25 g was chosen, due to the fact that no residuals were left into the vessels after digestion.

## **Full Factorial Design**

A full factorial design of 2<sup>5</sup> experiments in random order was carried out by STATGRAPHICS Centurion XV.I, to examine the basic parameters of the digestion procedure in two different levels (low and high). The parameters optimized were the volumes of HNO<sub>3</sub>, HF and HCl, temperature and hold time (**Table S2**). The chosen analytes haven to be representative of all being determined. Therefore, five analytes (Na, Fe, As, Se and Pb) were selected

for the design. These analytes included the entire range of  $m/z$  of the method (low:  $^{23}\text{Na}$ ; high:  $^{206-208}\text{Pb}$ ; middle:  $^{56}\text{Fe}$ ,  $^{75}\text{As}$ ,  $^{78}\text{Se}$ ) and all the analysis modes; no gas (Pb), He (As, Na) and  $\text{H}_2$  (Se, Fe). Furthermore, they included all the sectors of the periodic table (s: Na; p: As, Se, Pb; d: Fe) and finally had different properties (size, ionization energy, electron affinity, electron negativity, boiling point, affinity to chloride ions and solubility to different acids) characterizing them as metals (Na, Fe and Pb) metalloids (As) and non-metals (Se).

**Table S2** Variables and levels used in the full factorial design experiment

Variables	Low level (-)	High level (+)	Units
A. HCl	2	4	mL
B. $\text{HNO}_3$	2	4	mL
C. HF	2	3	mL
D. Hold time	5	10	min
E. Temperature	190	220	C

The influence of each parameter was evaluated using pareto charts (**Fig. S1**). The length of each bar is proportional to the value of a t-statistic calculated for the corresponding effect. Any bar beyond the vertical line (Standardized Effect >2.1) is statistically significant at the 95.0% coefficient level. Moreover, significances of the effects were checked by  $R^2$  of analysis of the variance (ANOVA). The statistic  $R^2$  was 81.5% for Na, 85.3% for Fe, 88.1% for As, 48.9% for Se and 76.5% for Pb.

Pareto charts showed that the most critical variables were: hold time (+), temperature (+) and volume of HCl (-) for Na; hold time (+) and temperature (+) for Fe; hold time (+), temperature (+) and volumes of HCl (+) and  $\text{HNO}_3$  (-) for As; temperature (+) for Pb; and none for Se. Additionally, significant interactions were emphasized between hold time and temperature (-) for Na, Fe, Pb and As and hold time with volume of HCl (+), temperature with volume of  $\text{HNO}_3$  (-), volumes of HCl and  $\text{HNO}_3$  (-) for As. The symbols (+) and (-) represent the high and the low level, respectively (**Fig. S1**).

The lines of Main Effect Plots (**Fig. S2**) indicate the estimated change in analytes as each variable was moved from its low level to its high level, with

all other variables held constant at a value midway between their lows and their highs. The variables with significant main effects have a bigger impact on the response than the others. Main Effects Plots showed that for the non-significant variables (HF and HNO<sub>3</sub>), the higher response was given from the low level.

The correlations between the variables that have an important impact on each analyte were showed by the Interaction Plots (**Fig. S3**). Only the low temperature level demonstrated a significant interaction with the time for As, Na and Fe, while for Pb both levels showed this. The response of As, Na and Fe was greater when the upper level of time influenced with temperature, that is in low temperature the system needs more time to obtain the maximum response. Also, for As the high level of time and the low level of HNO<sub>3</sub> showed important interactions with HCl and the high level of temperature demonstrated a significant interaction with HNO<sub>3</sub>. The higher response of As was obtained when the low level of temperature applied in conjunction with the low level of HNO<sub>3</sub> and the high level of HCl affected by the high level of time and the low level of HNO<sub>3</sub>.

### **Central Composite Design**

Having concluded to the critical variables with the screening experiments, a rotatable and orthogonal central composite design (CCD) 2<sup>3</sup> + star point, consisting of 23 experiments in random order was followed. The response variables were the volume of HCl, the hold time and the temperature (**Table S3**). For the non-critical parameters, HNO<sub>3</sub> and HF, their low level was used, namely 2 mL each. From the Main Effects Plots of CCD, the optimum values of the significant parameters for each analyte were derived. The optimum value for HCl volume was 5.5 mL, because Na, As and Pb produced the maximum response at that value. The element that gave low response value at this value was Se, however HCl volume was found not critical by the screening experiments. The interaction between hold time and temperature was shown in “Estimated Response Surface” plots (**Fig. S4**). The optimum values for Na did not coincide with the optimum ones of the other elements and therefore it was necessary to perform multiple response optimizations. Multiple response optimizations were performed in order to achieve best

compromised response for all analytes simultaneously, combined in one function (namely the Desirability Plot). In summary, the optimum values of all variables for the digestion of mastic gum are shown in **Table S4**.

**Table S3** Variables and applied levels of CCD

Variables	Levels					Units
	-a	-1	0	+1	+a	
HCl	0.5	1.5	3.0	4.5	5.5	mL
Hold time	5	7	10	13	15	min
Temperature	200	210	220	230	240	C

**Table S4** Instrumental settings of the Mars X type microwave oven and optimum values of the digestion variables

Variable	Value
Power	1600 W (80%)
Pressure	400 psi
Ramp time	15 min
Hold time	7 min
Temperature	203 °C
mass	0.25 g
HCl	5.5 mL
HNO <sub>3</sub>	2 mL
HF	2 mL

Dilution to a final volume of 20 mL with ultra-pure water

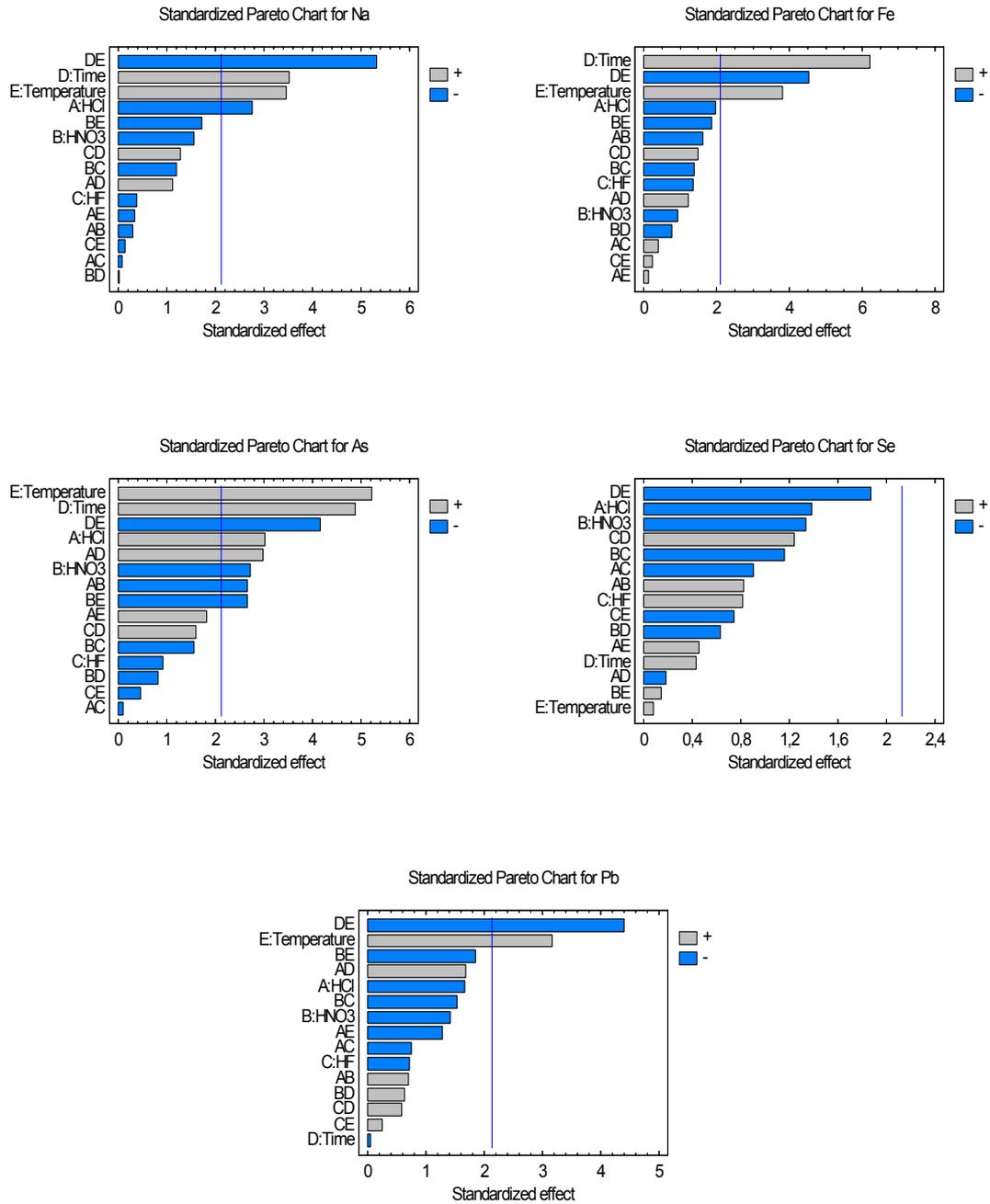
## Conclusions

A full factorial design of 2<sup>5</sup> experiments was performed in order to screen the factors that affect the microwave assisted acid digestion of mastic gum. The most critical parameters were digestion temperature, hold time and the volume of HCl. The sample mass should be restricted to 0.25 g for complete decomposition. This step played a significant role because such matrices (resins) are hard to be dissolved and therefore, accurate quantification is difficult. The proposed digestion procedure is efficient for complex matrices containing Si, S, P, C, Cl and F, as major matrix elements.

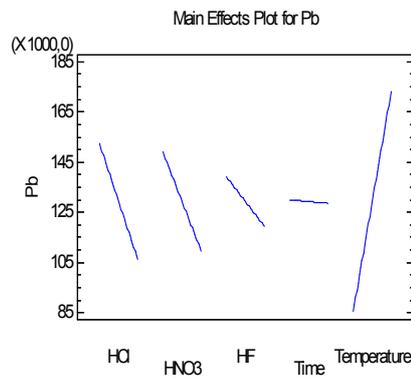
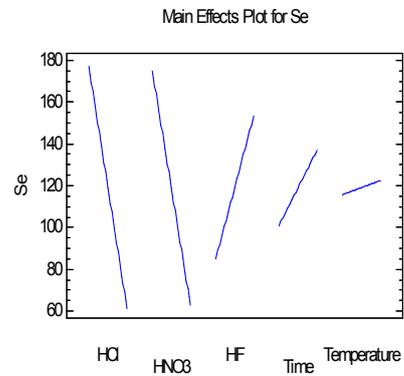
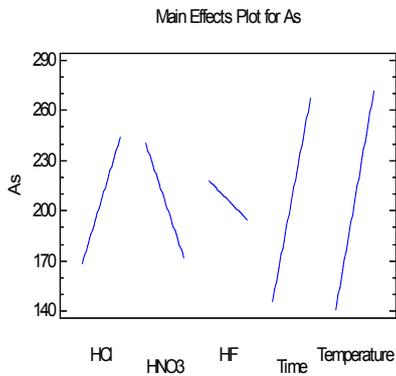
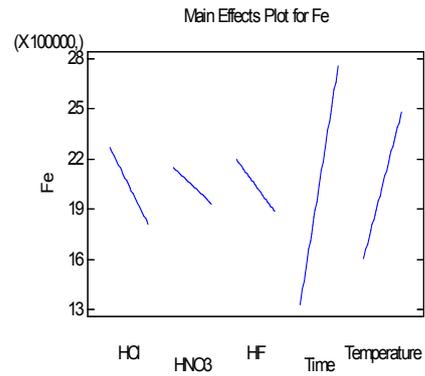
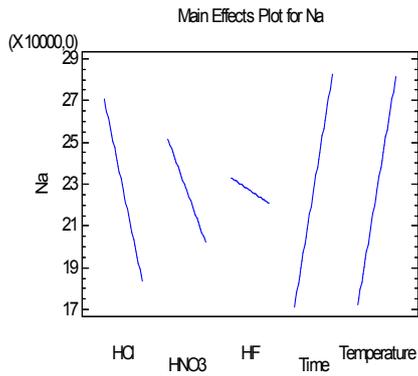
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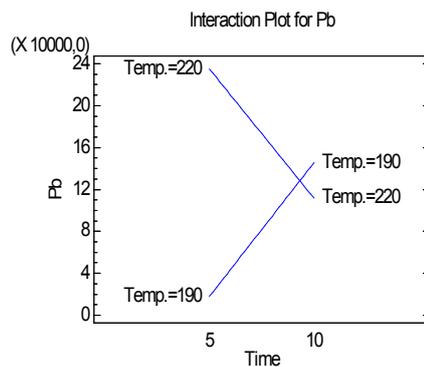
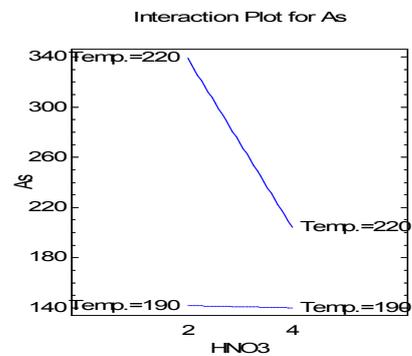
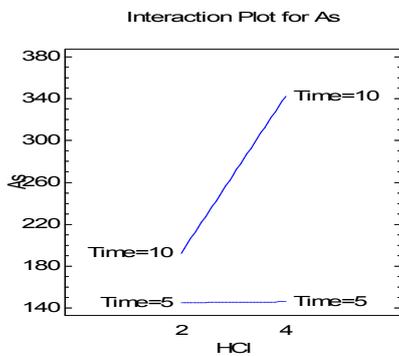
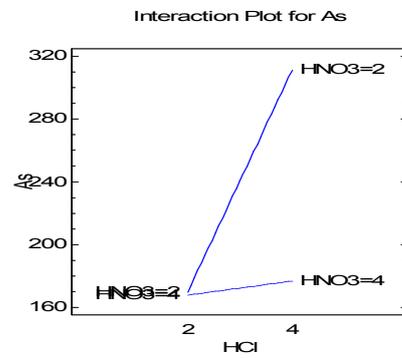
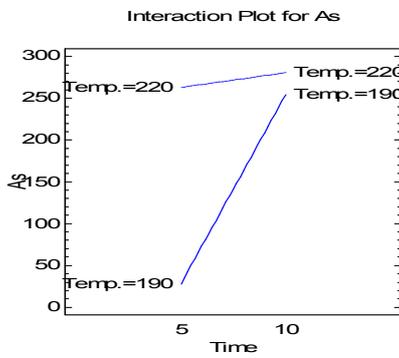
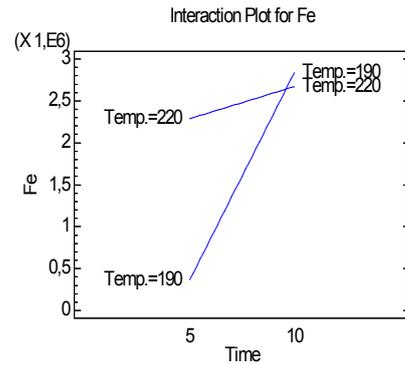
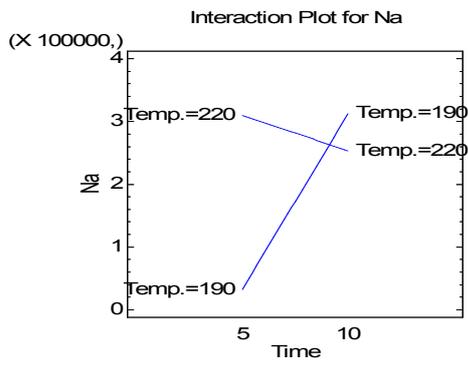
**Fig. S1.** Standardized pareto charts from screening experiments.



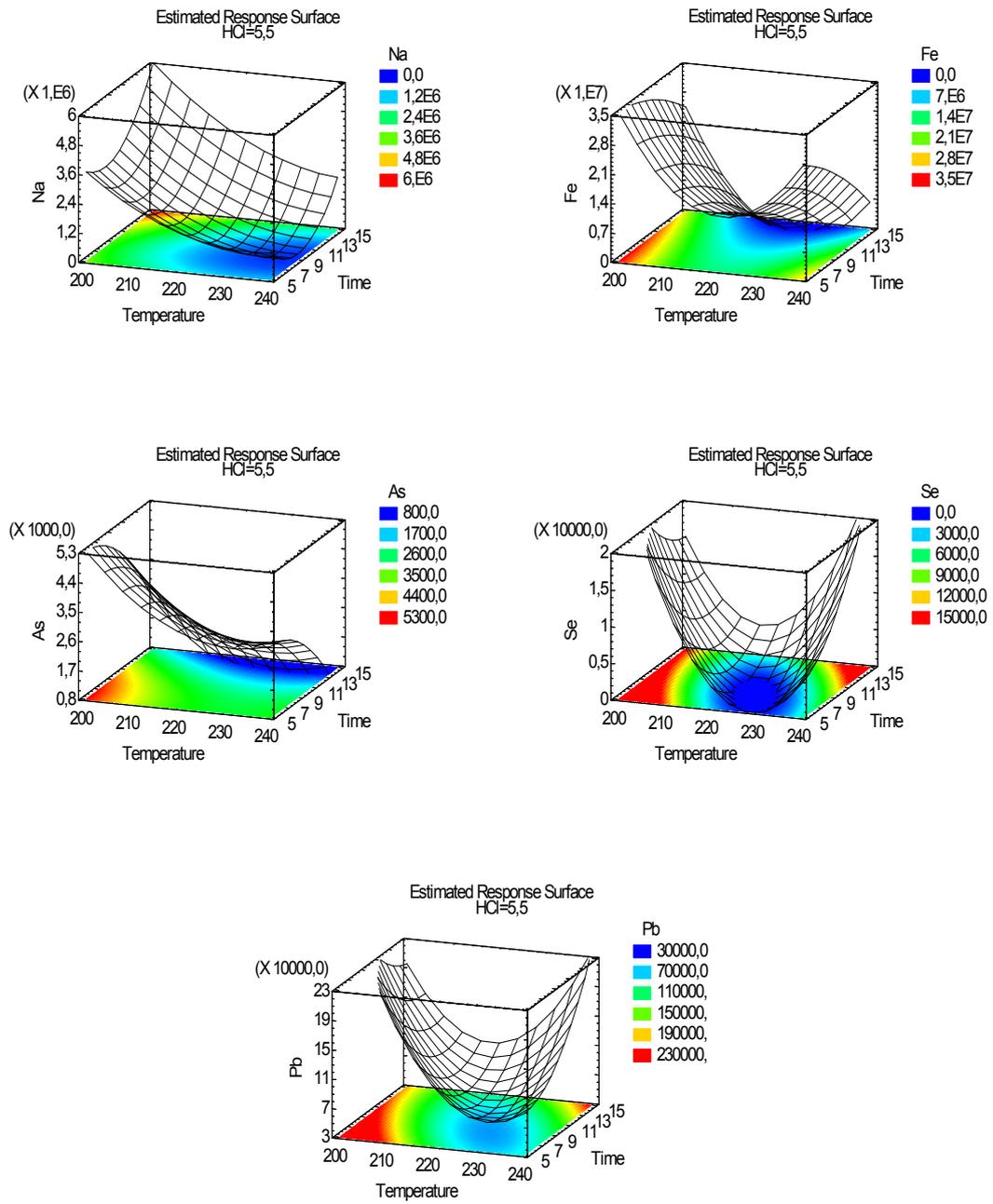
**Fig. S2.** Main effects plots from screening experiments.



**Fig. S3.** Interaction plots from screening experiments.

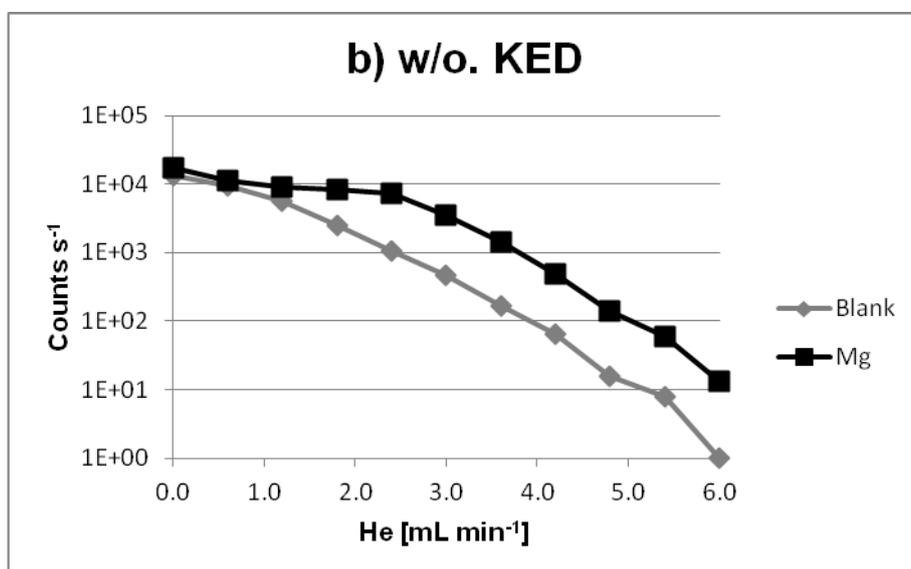
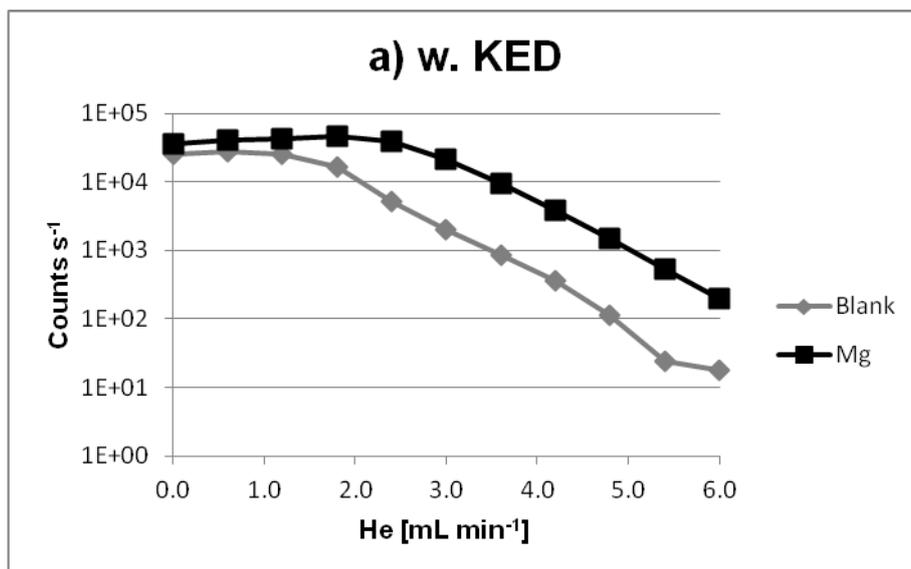


**Fig. S4.** Estimated response surfaces of Na, Fe, As, Se and Pb at 5.5 mL HCl.

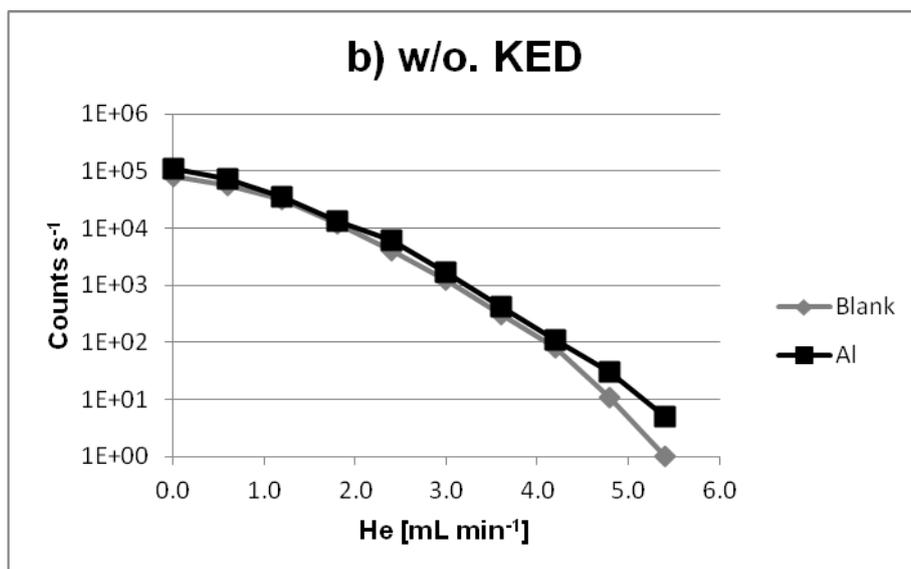
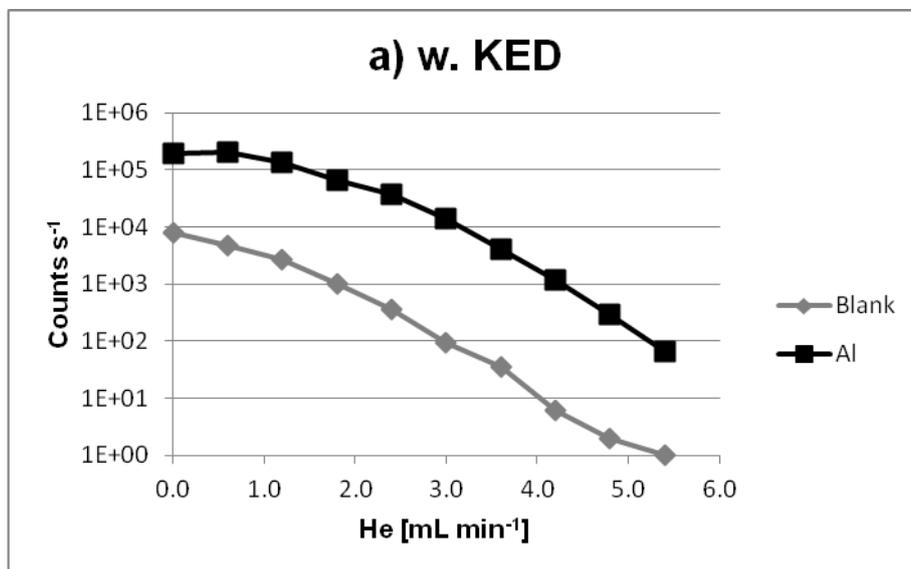


**Fig.S5.** Signal intensities of all elements and their interferences (blank) as a function of He flow rate: a) w. KED and b) w/o. KED.

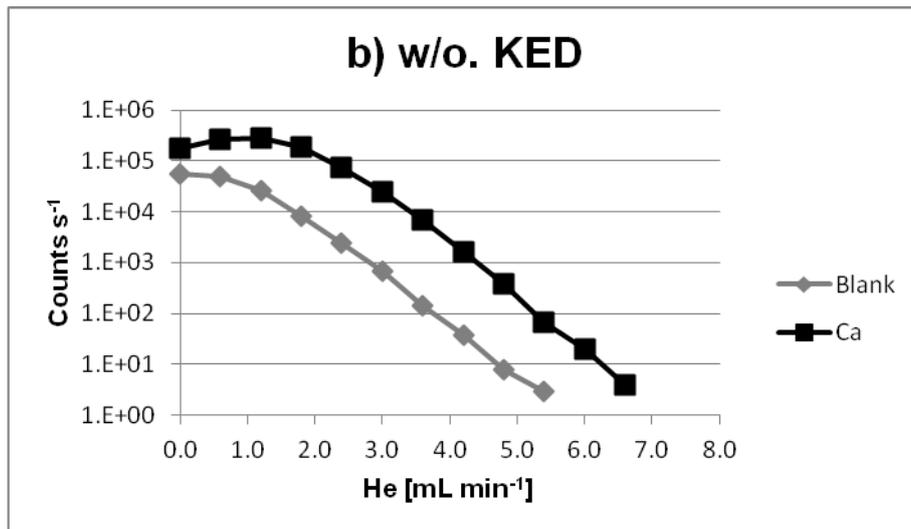
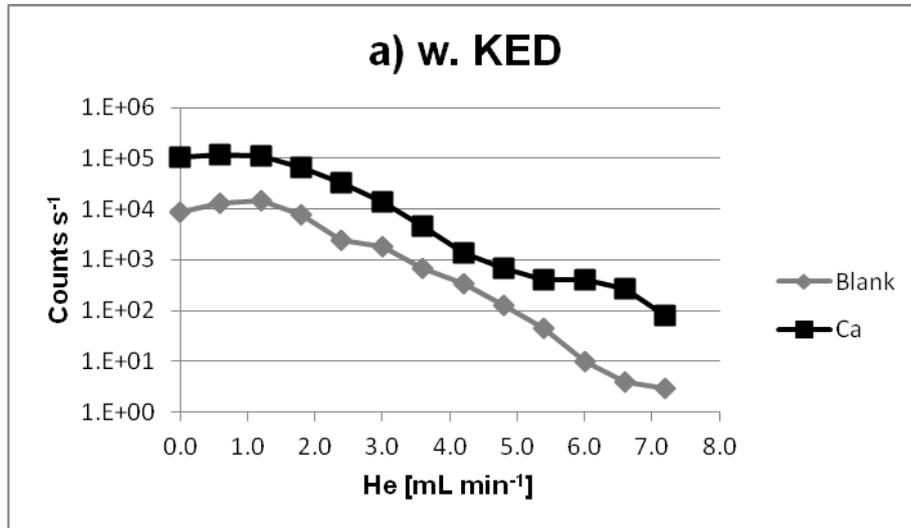
$^{24}\text{Mg}^+$



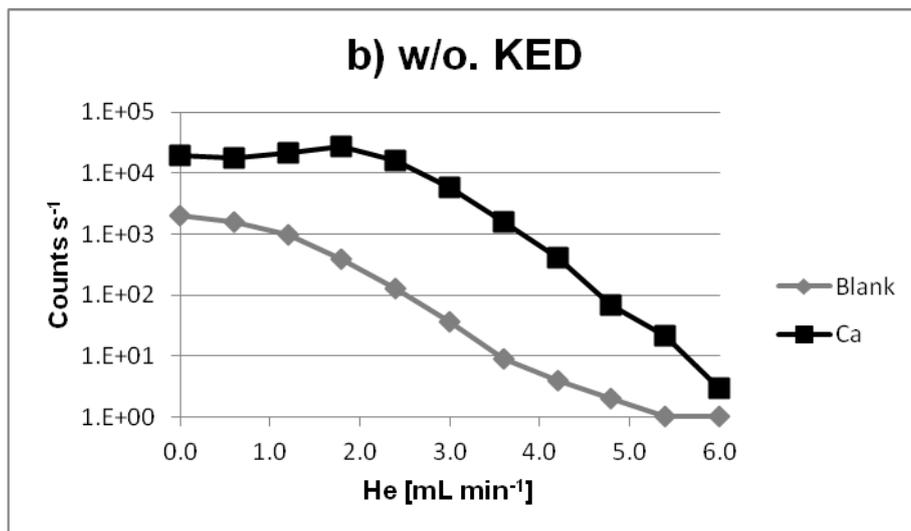
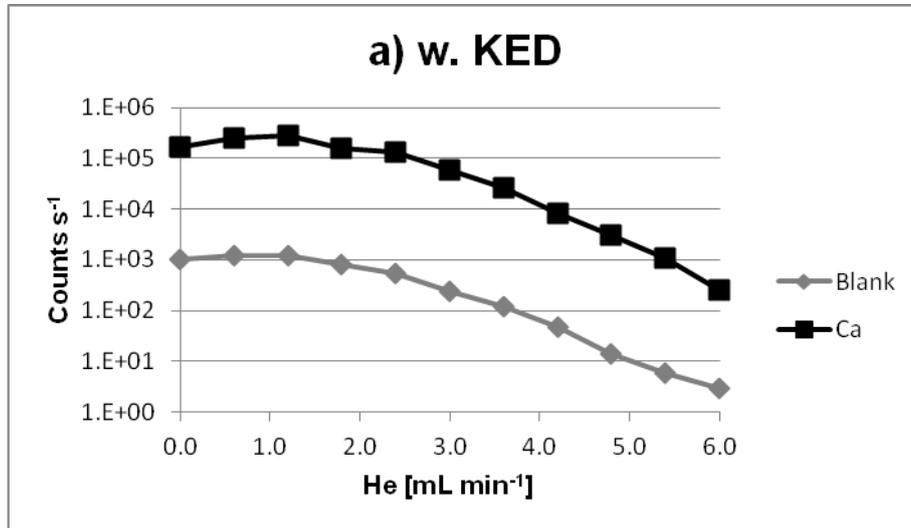
$^{27}\text{Al}^+$



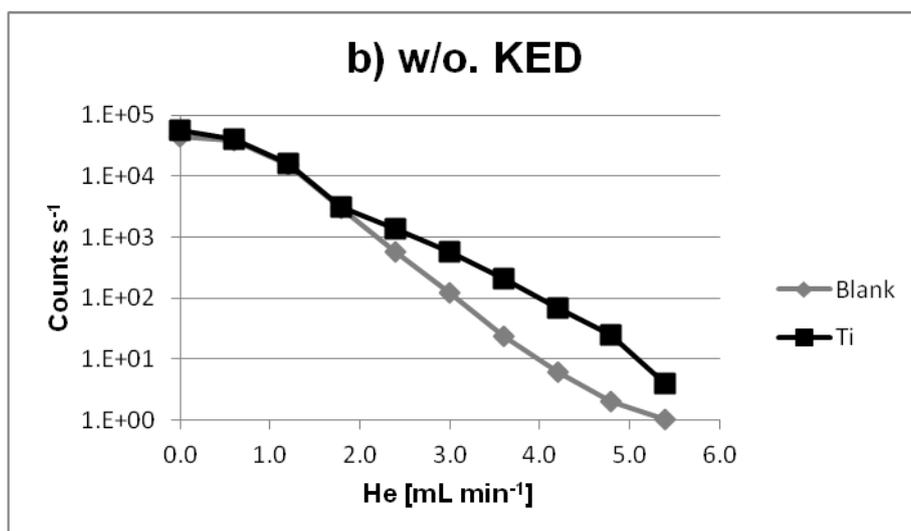
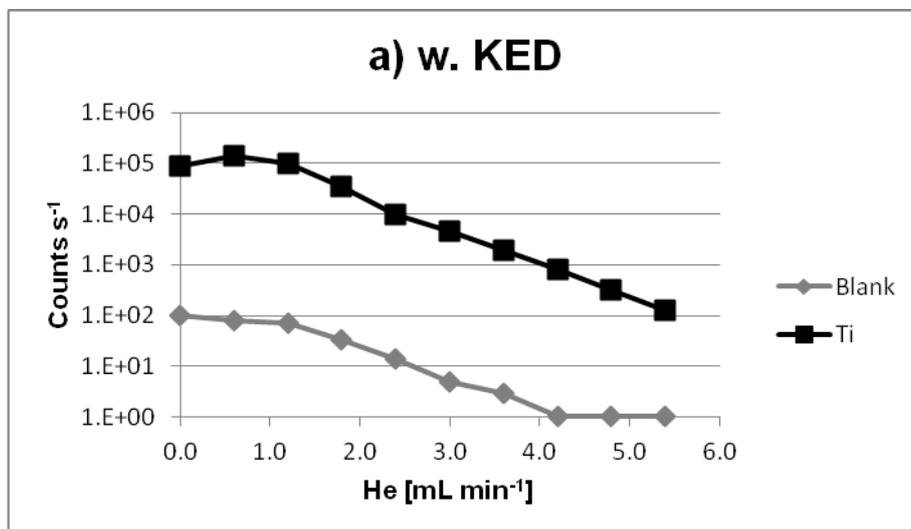
$^{42}\text{Ca}^+$



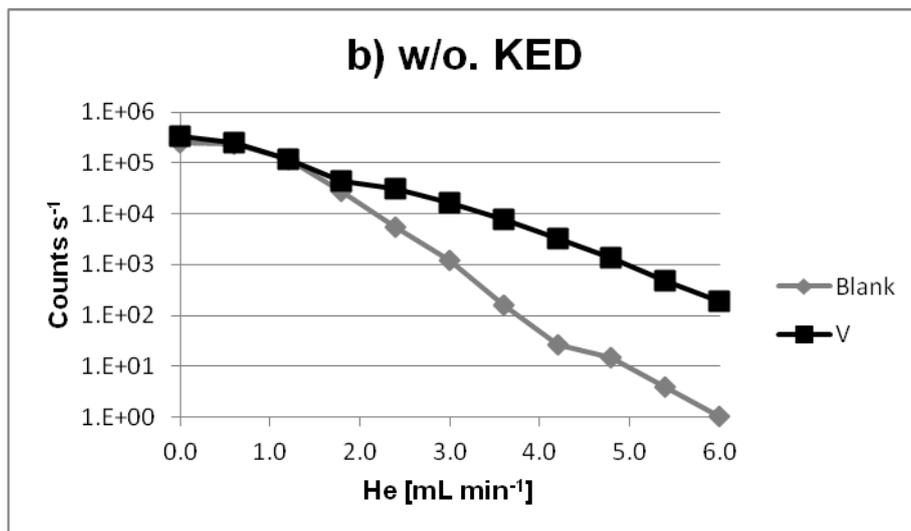
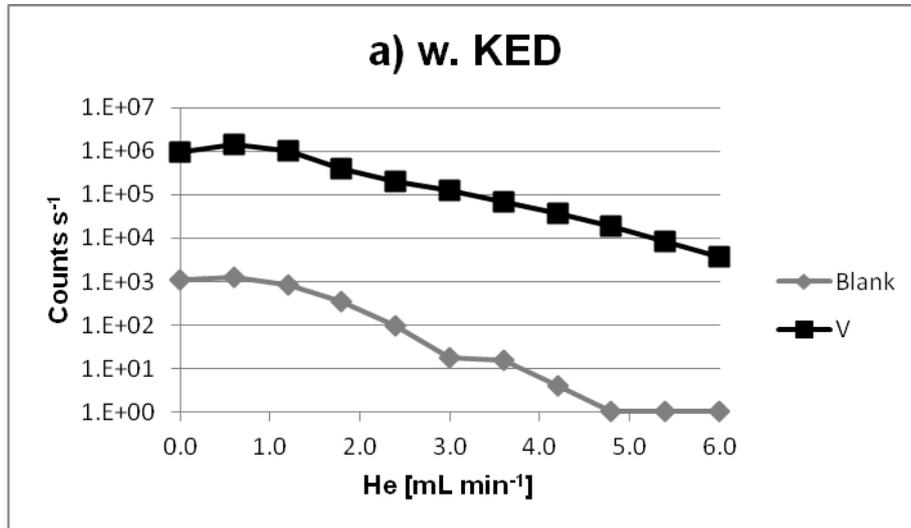
$^{43}\text{Ca}^+$

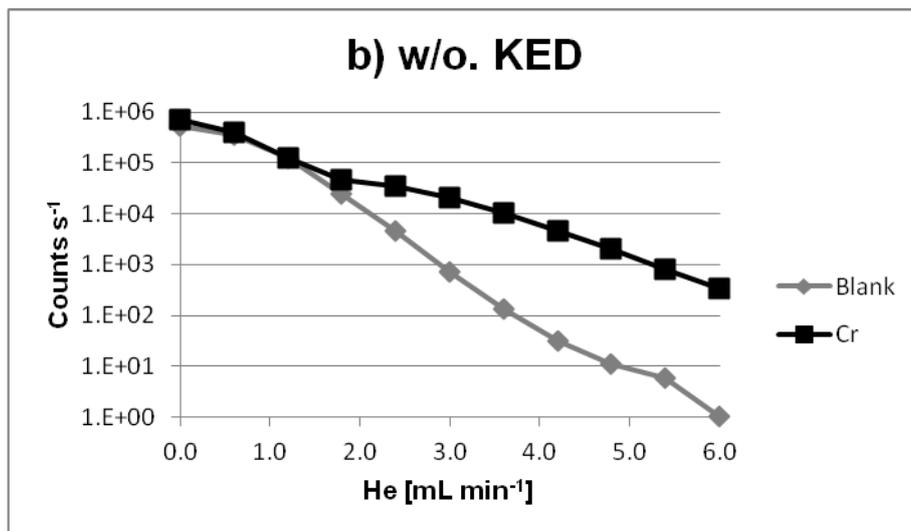
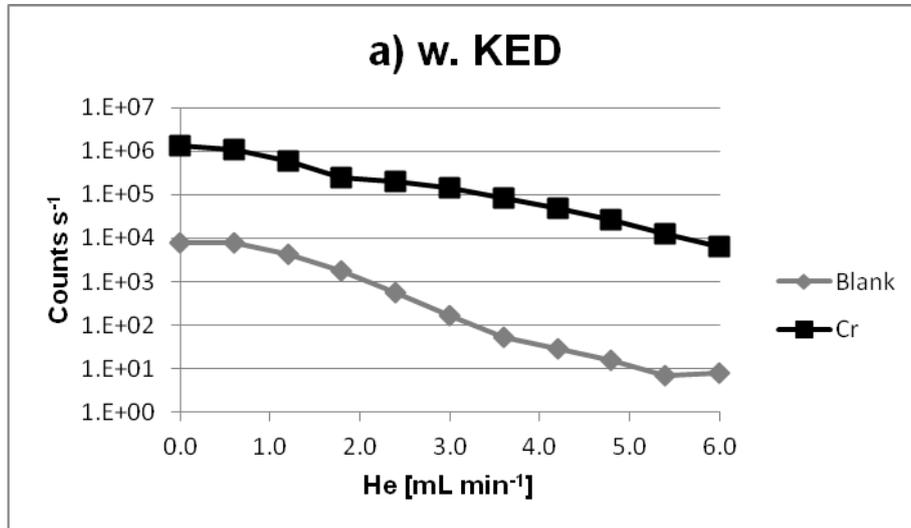


$^{47}\text{Ti}^+$

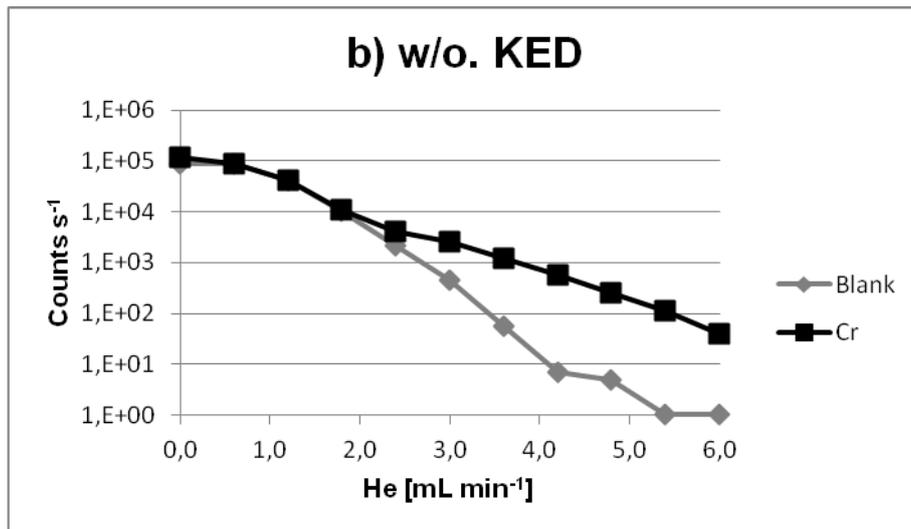
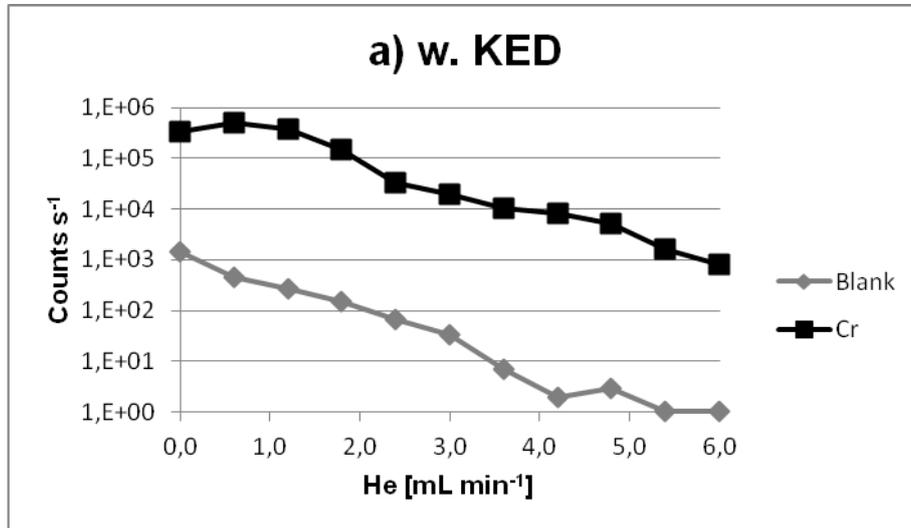


$^{51}\text{V}^+$

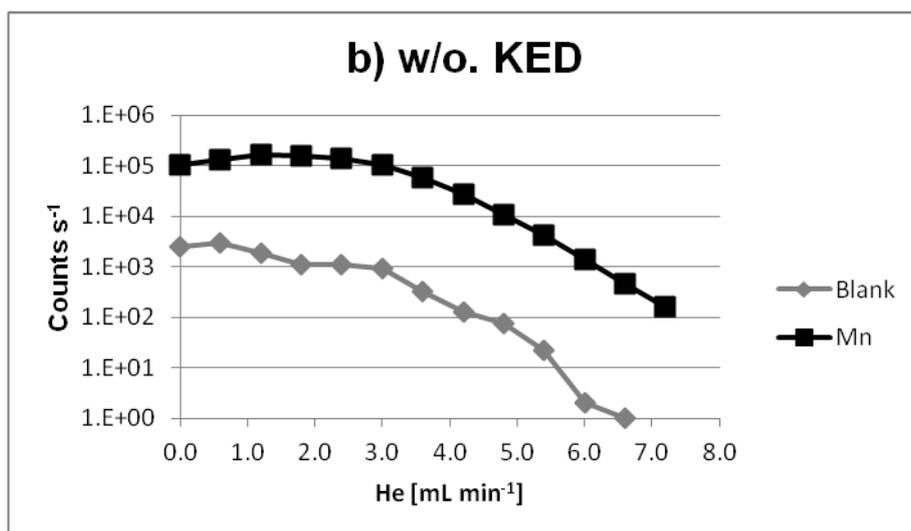
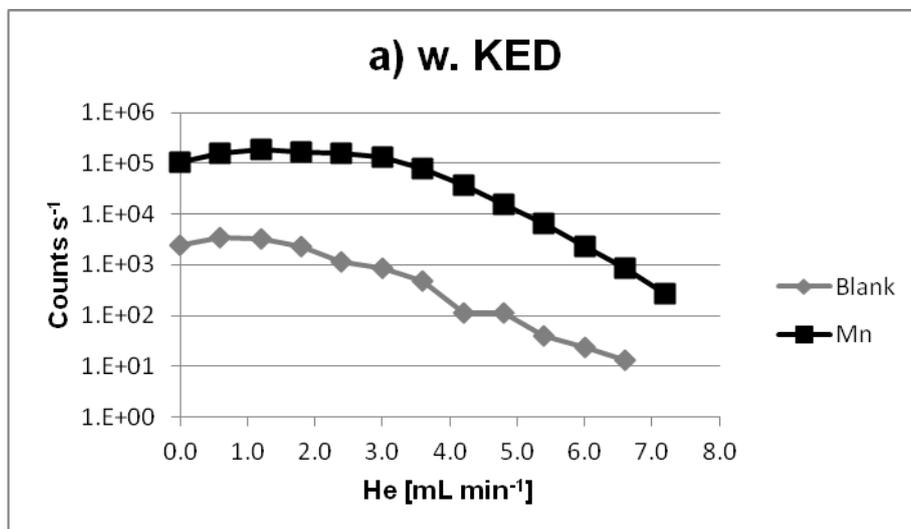




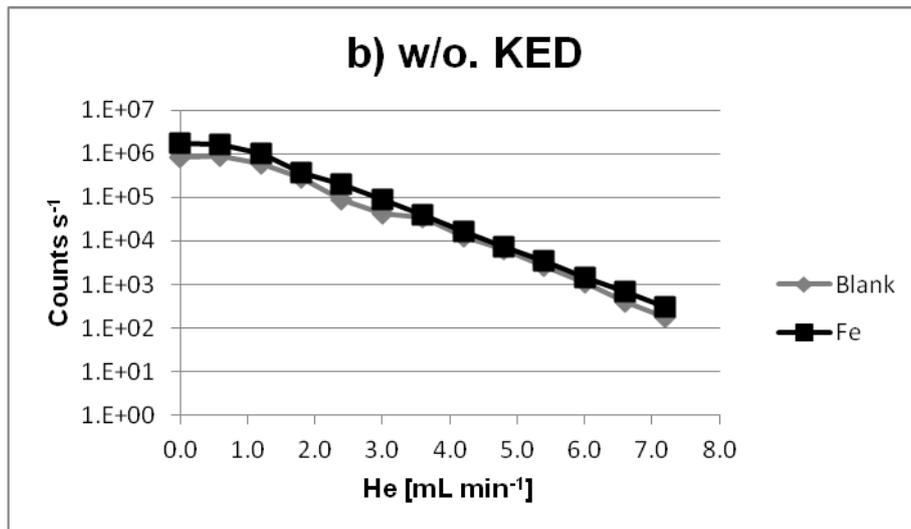
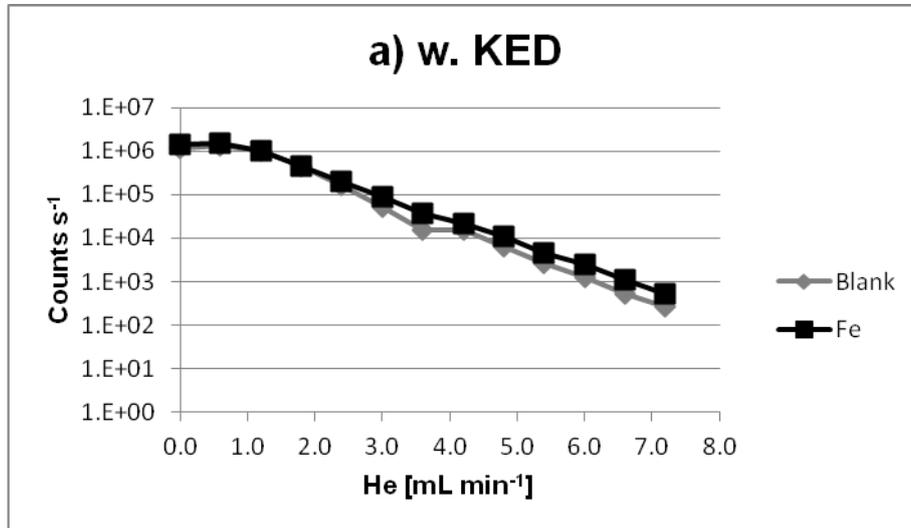
$^{53}\text{Cr}^+$



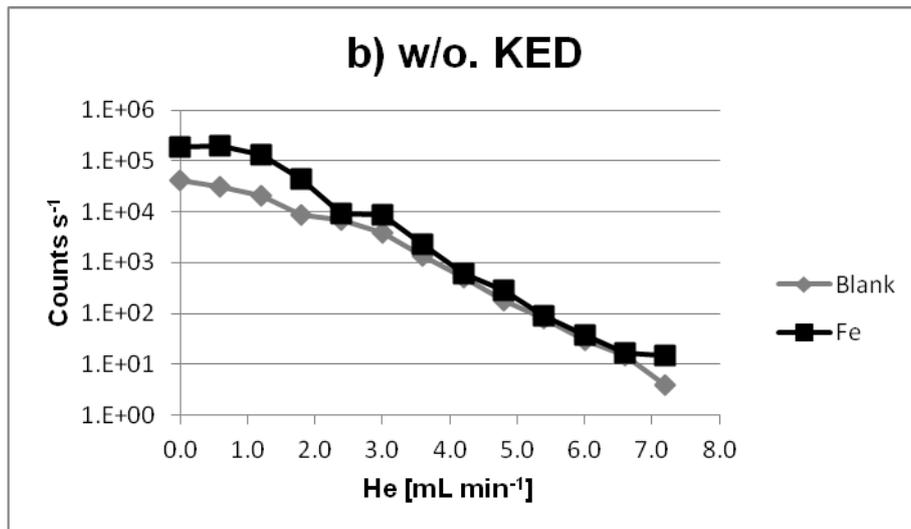
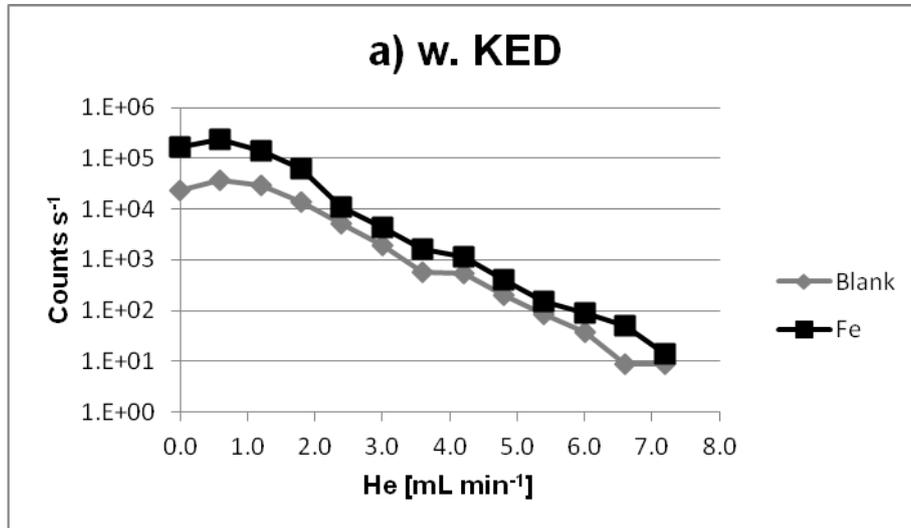
$^{55}\text{Mn}^+$



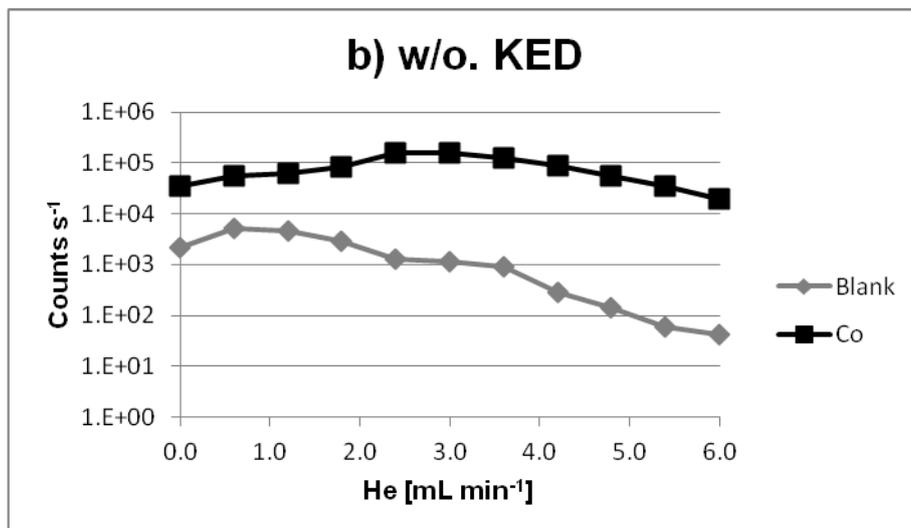
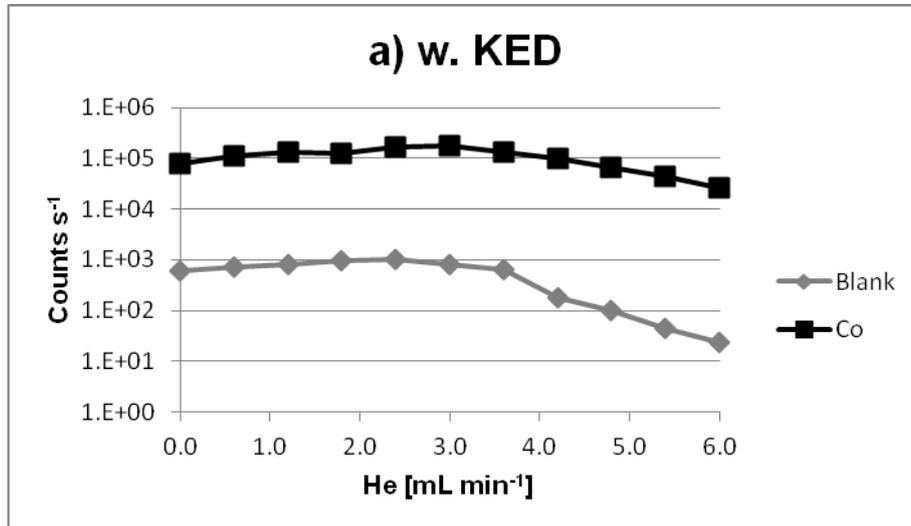
$^{56}\text{Fe}^+$



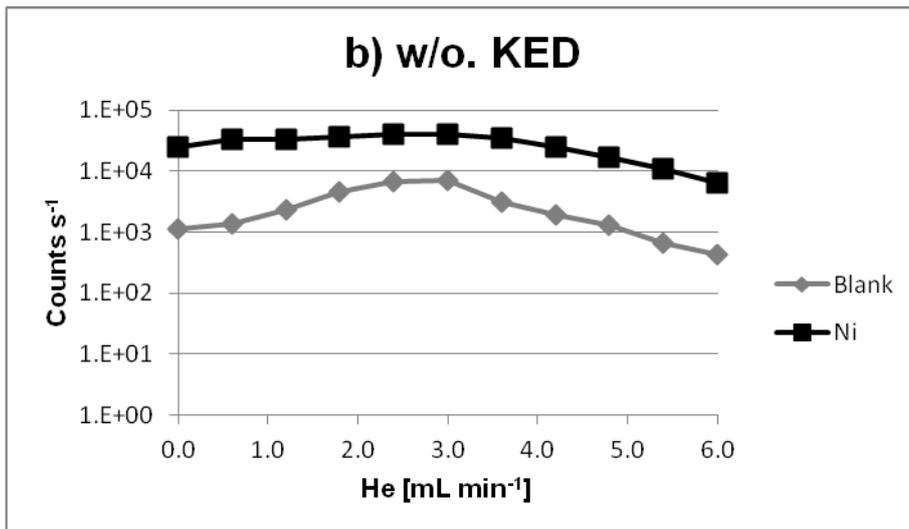
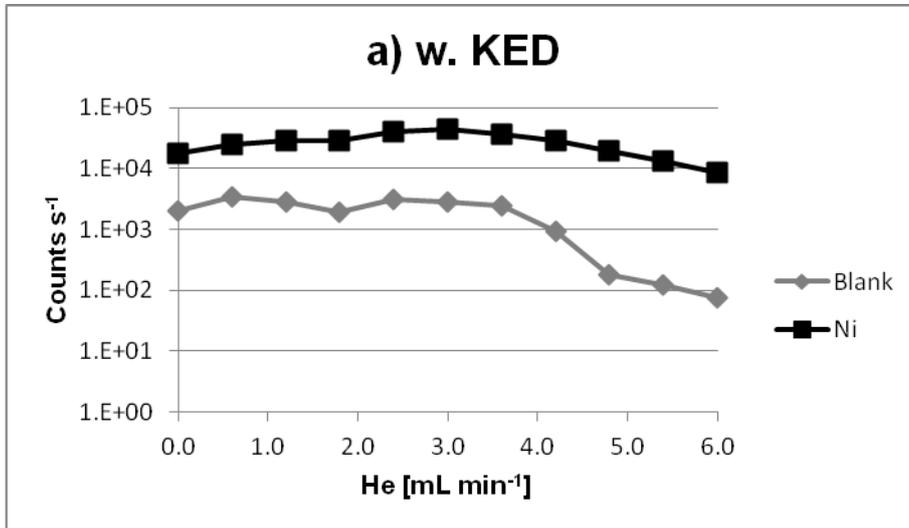
$^{57}\text{Fe}^+$



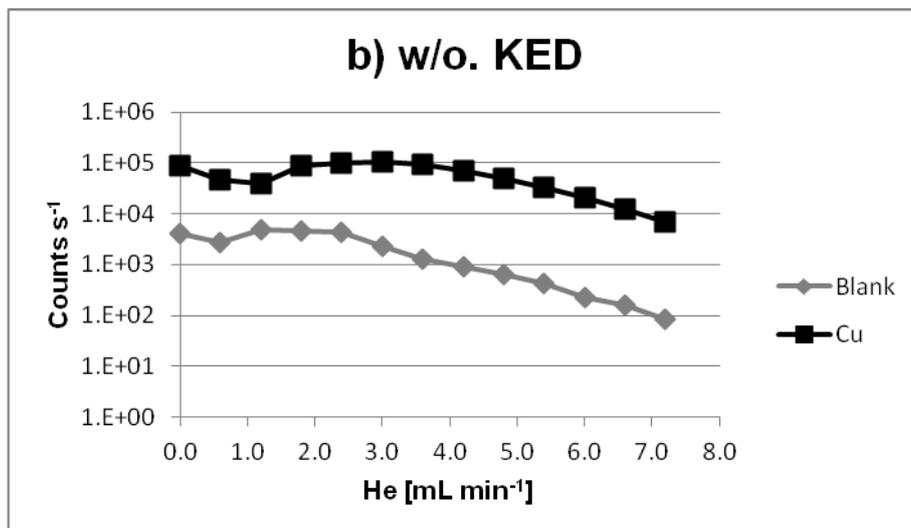
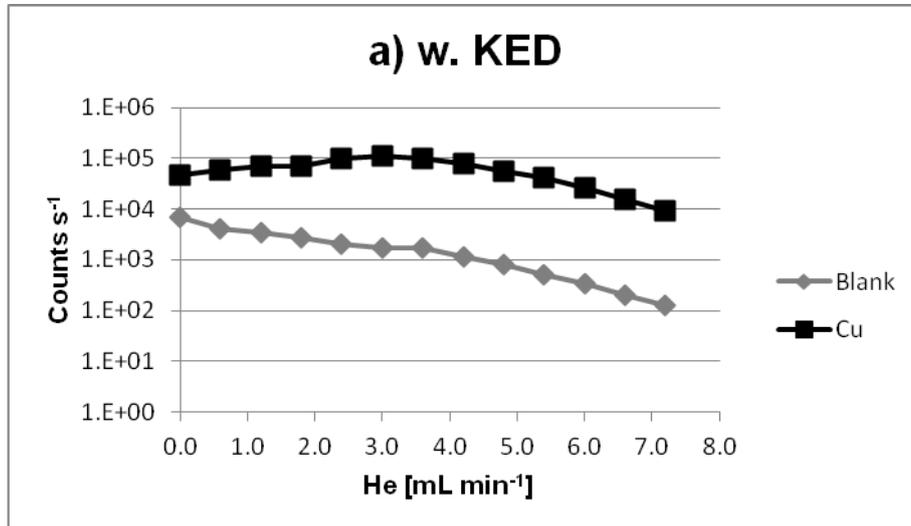
$^{59}\text{Co}^+$



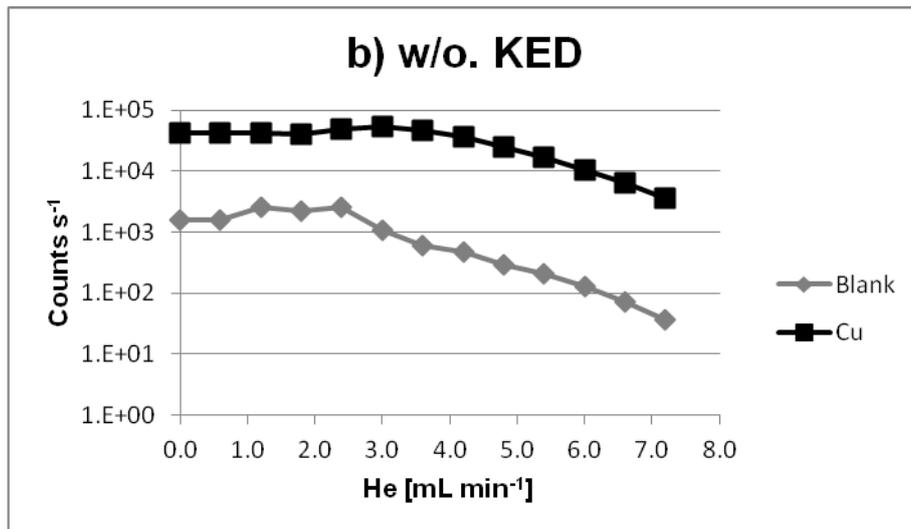
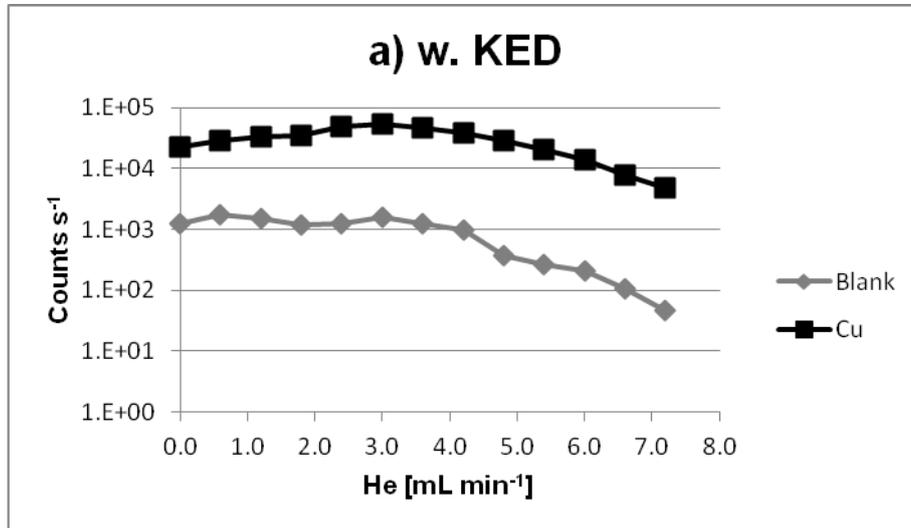
$^{60}\text{Ni}^+$



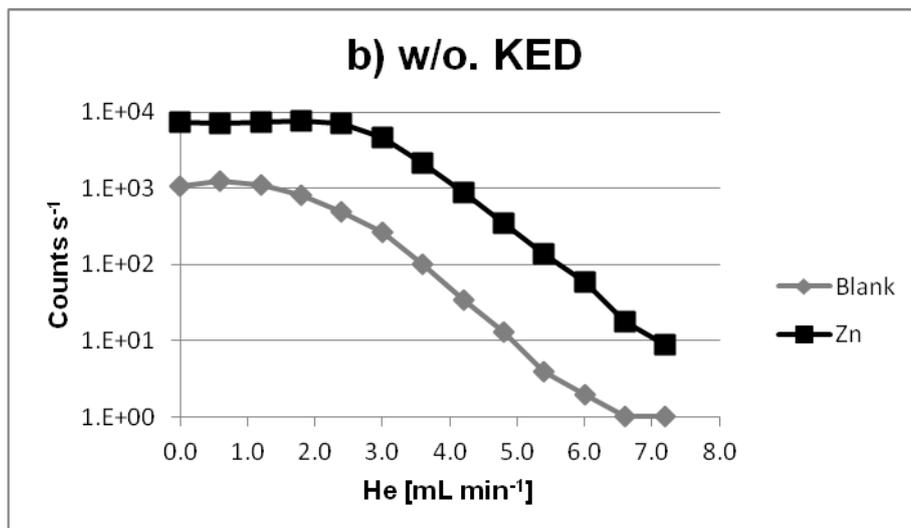
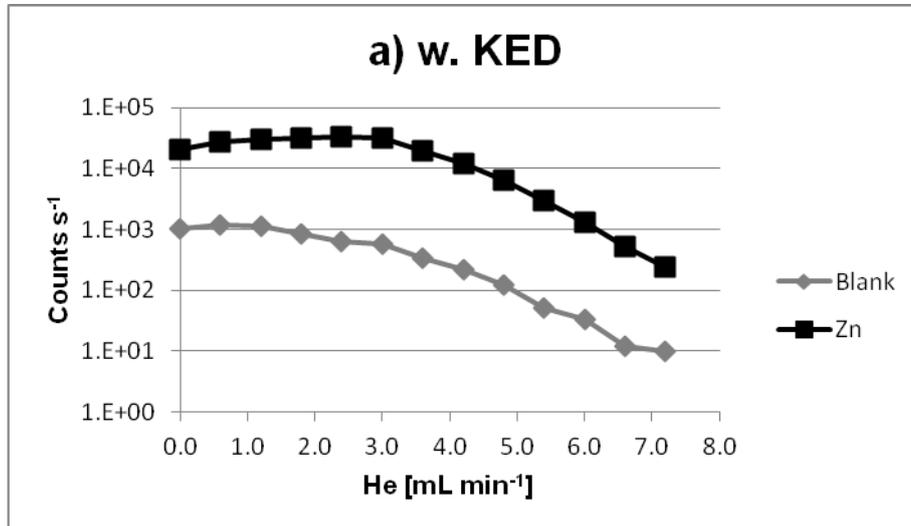
$^{63}\text{Cu}^+$



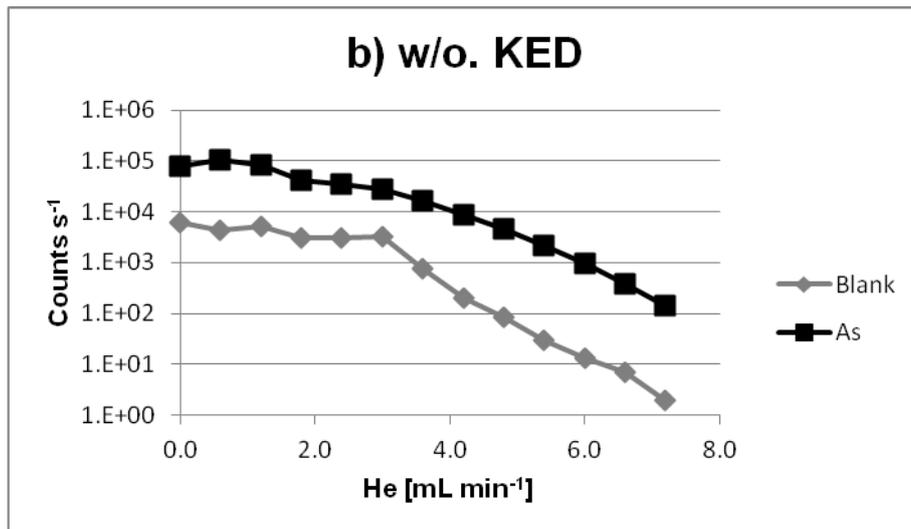
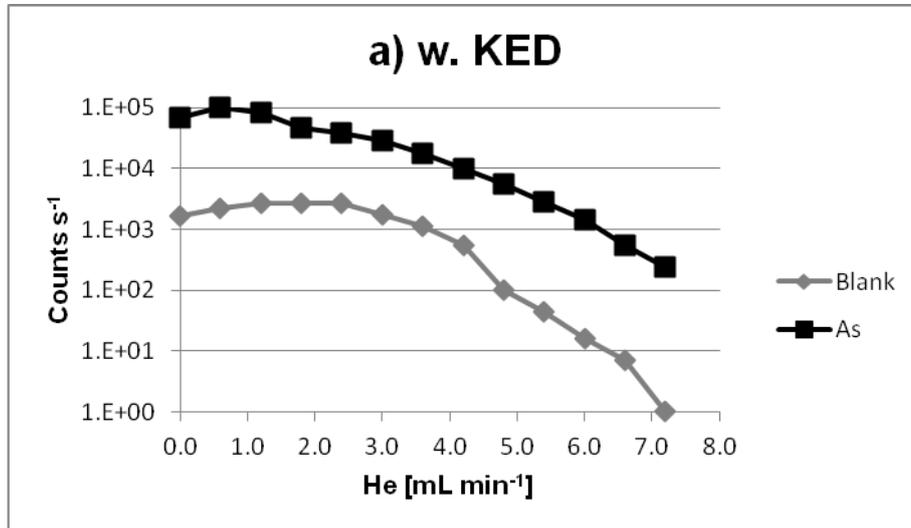
$^{65}\text{Cu}^+$



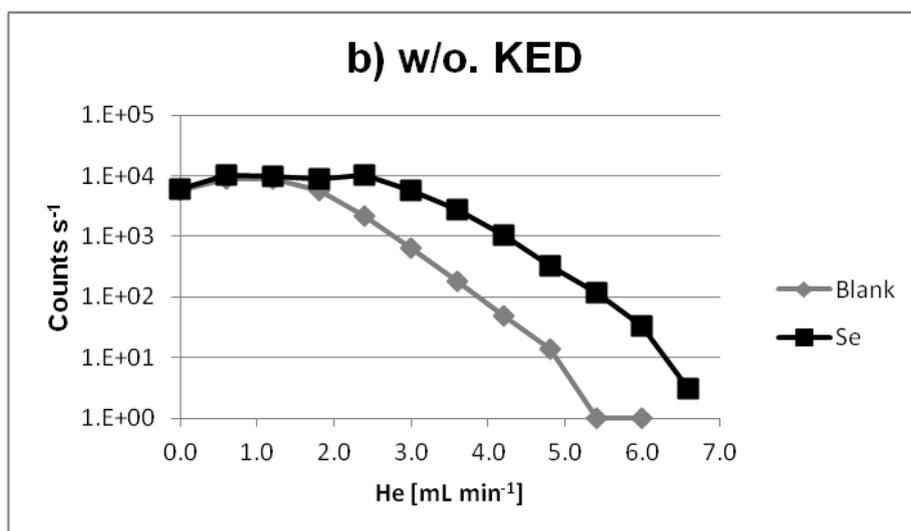
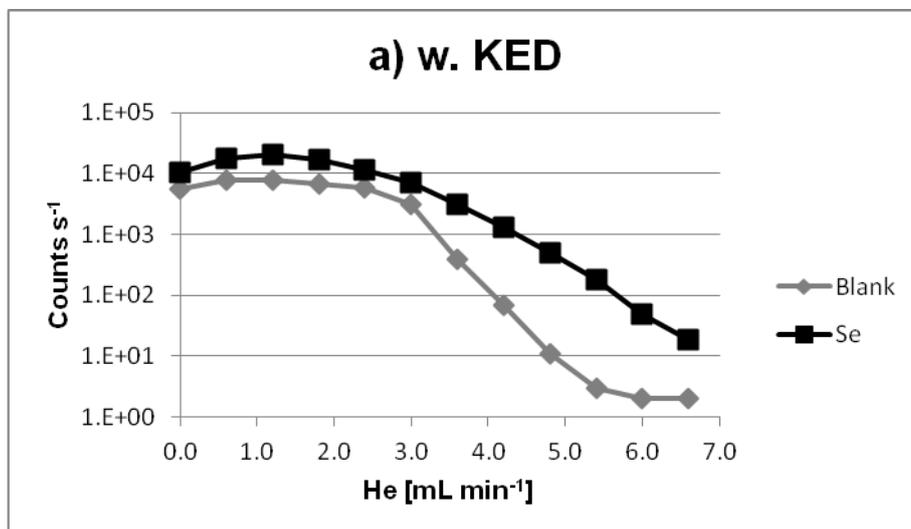
$^{66}\text{Zn}^+$



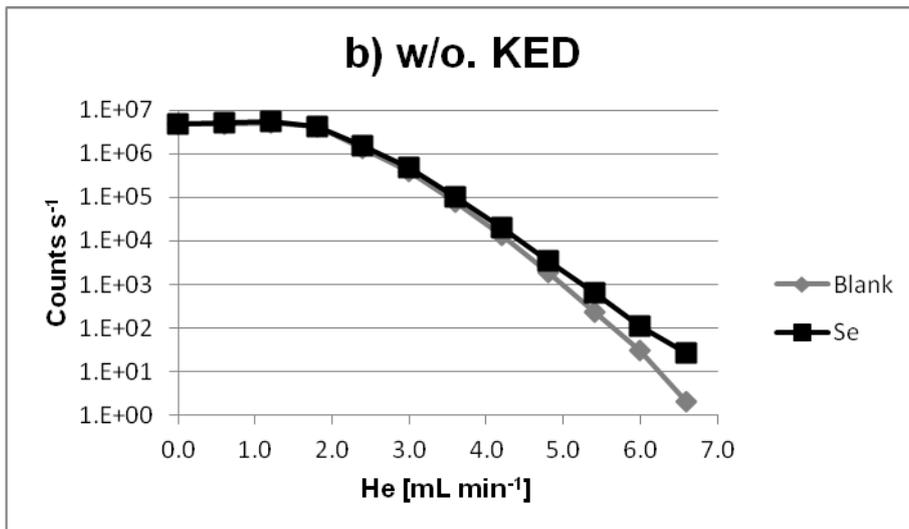
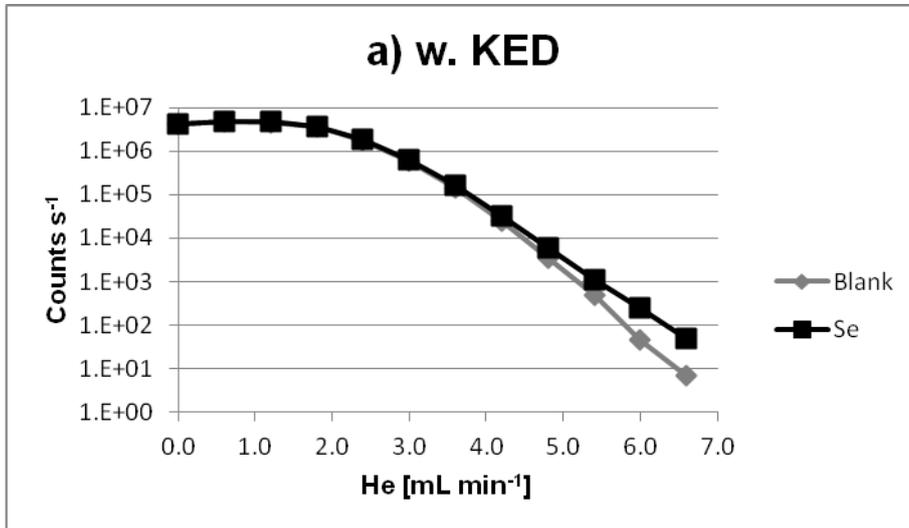
$^{75}\text{As}^+$



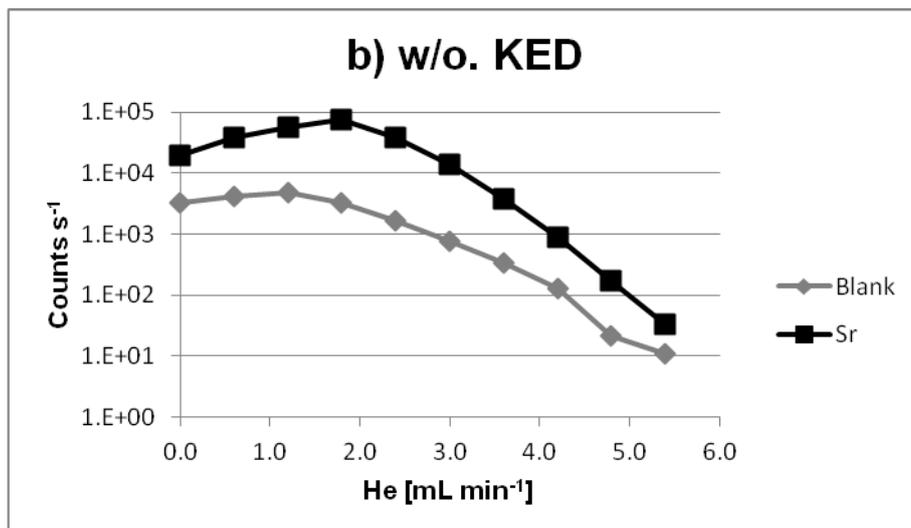
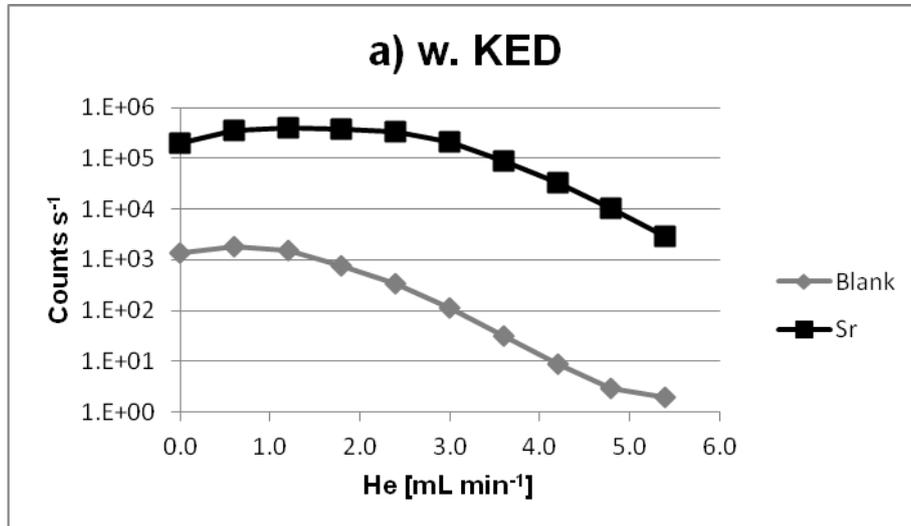
$^{78}\text{Se}^+$



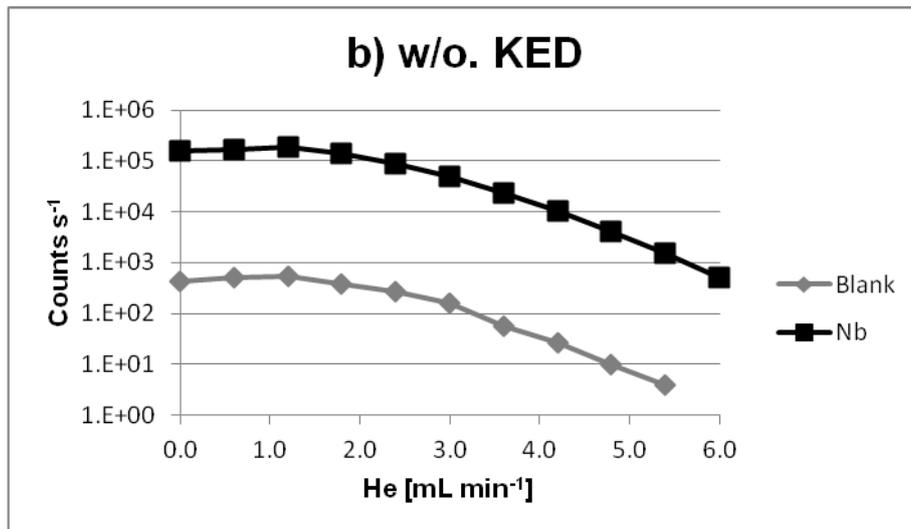
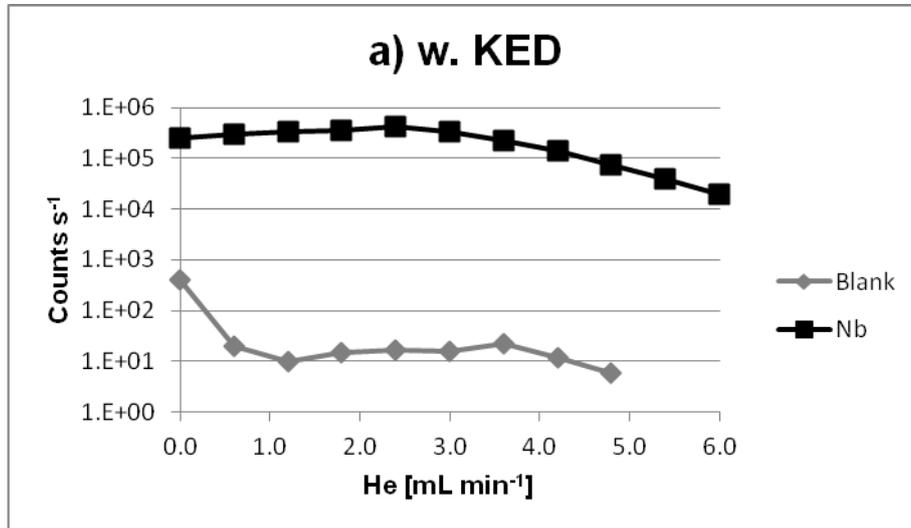
$^{80}\text{Se}^+$



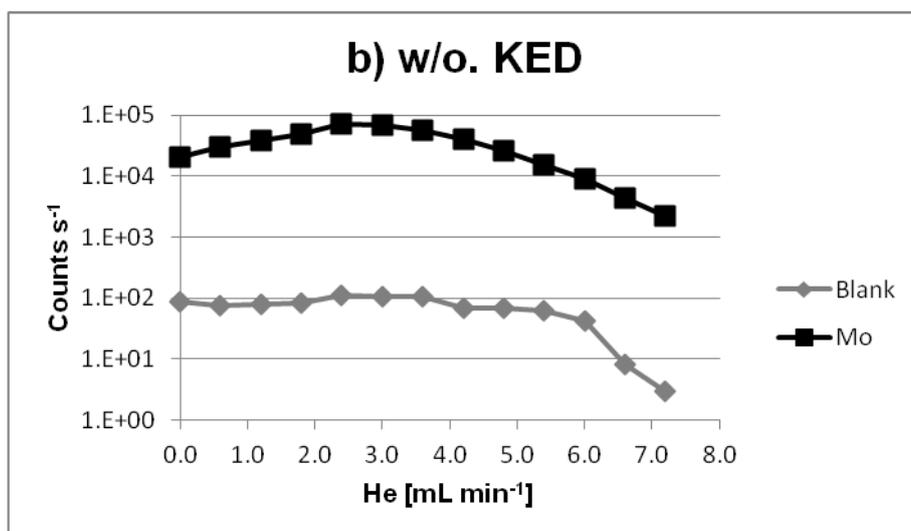
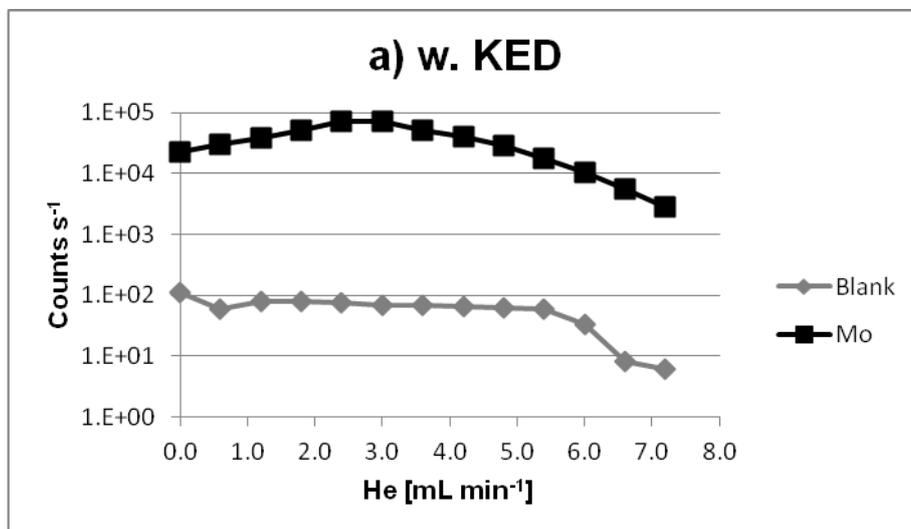
$^{88}\text{Sr}^+$



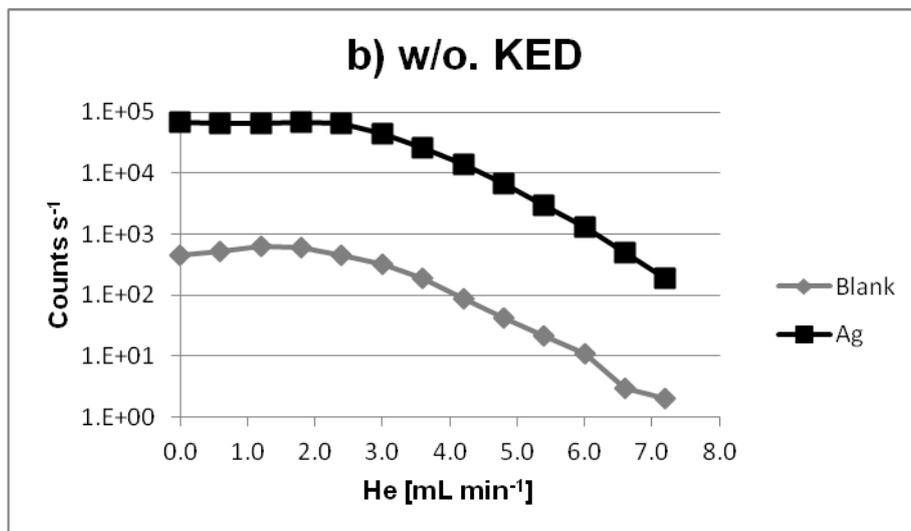
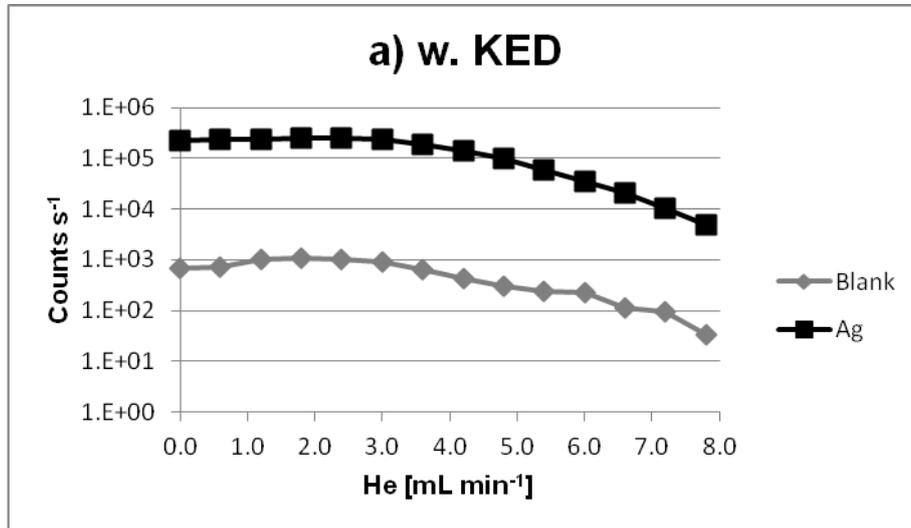
$^{93}\text{Nb}^+$



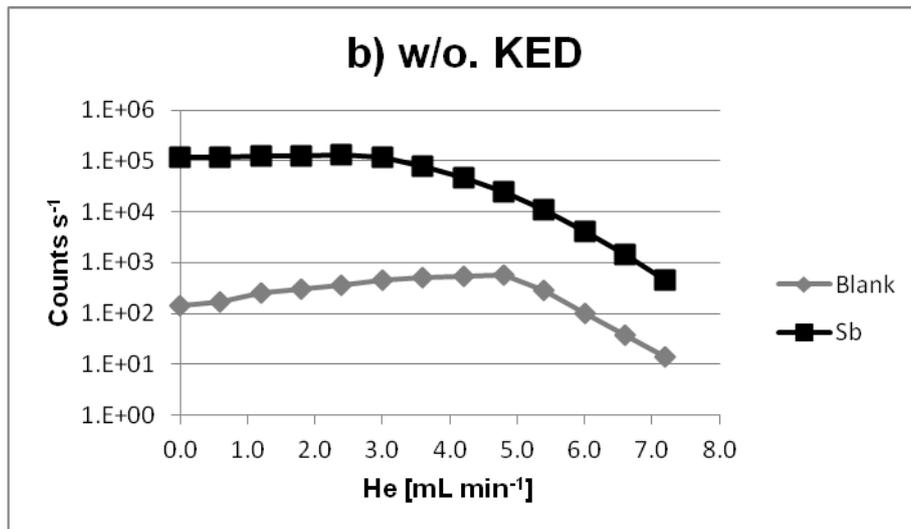
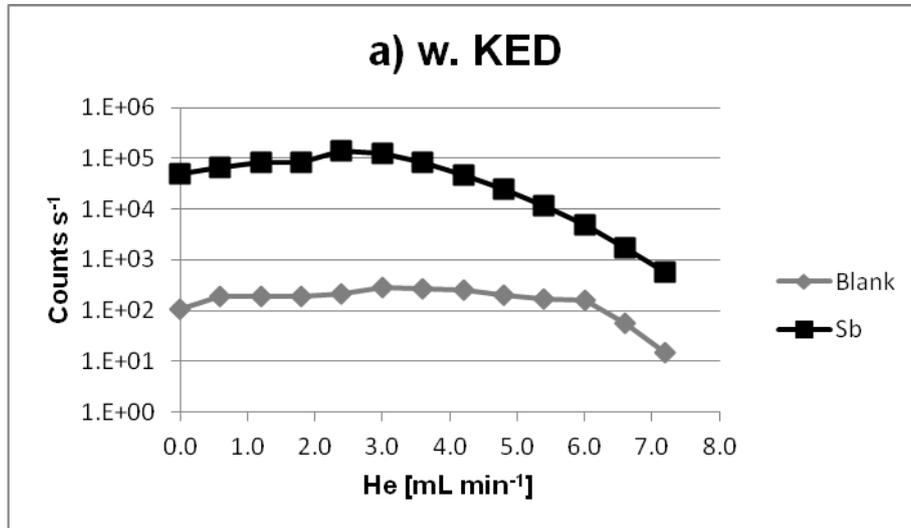
$^{95}\text{Mo}^+$



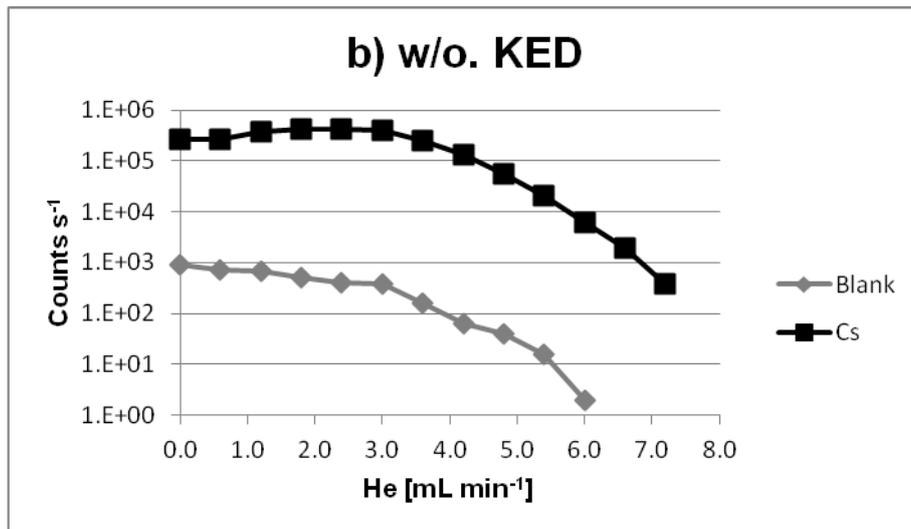
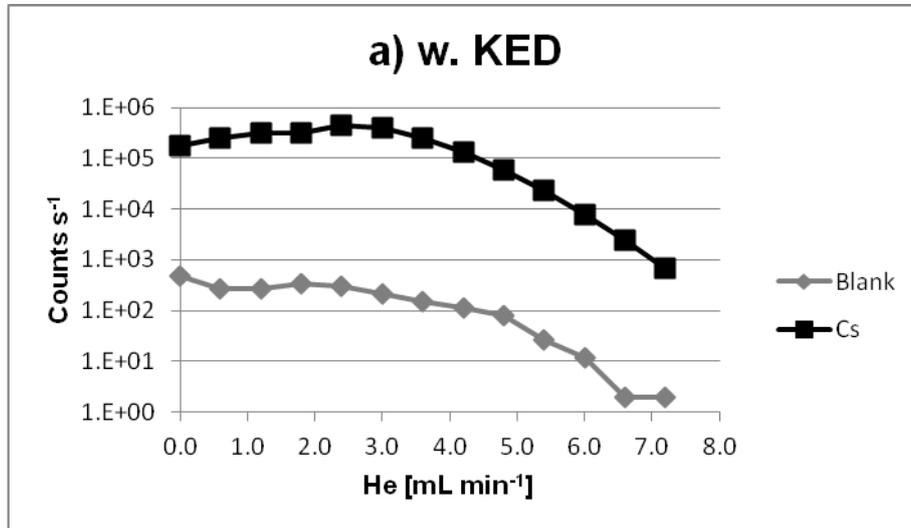
$^{107}\text{Ag}^+$



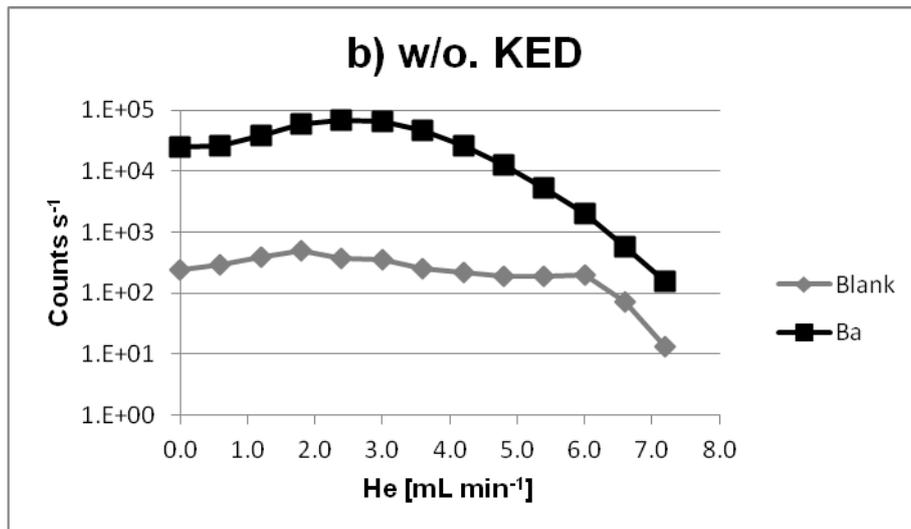
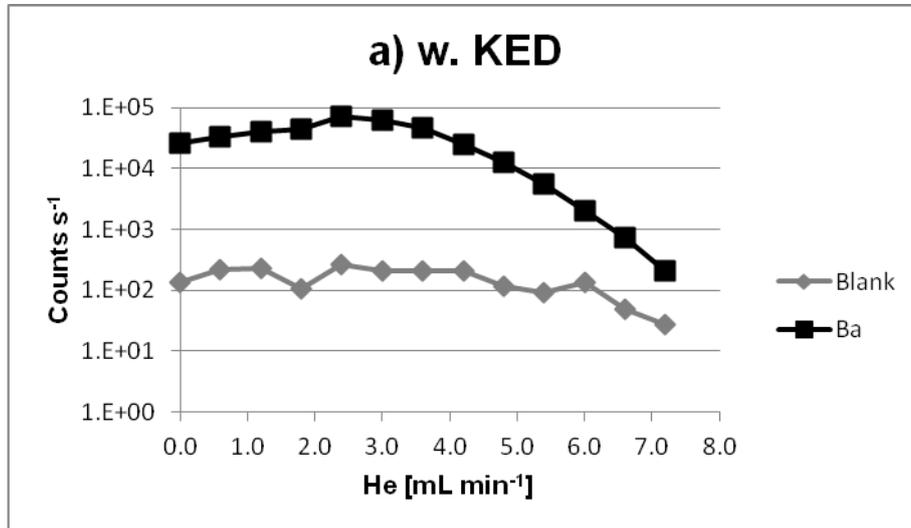
$^{121}\text{Sb}^+$



$^{133}\text{Cs}^+$

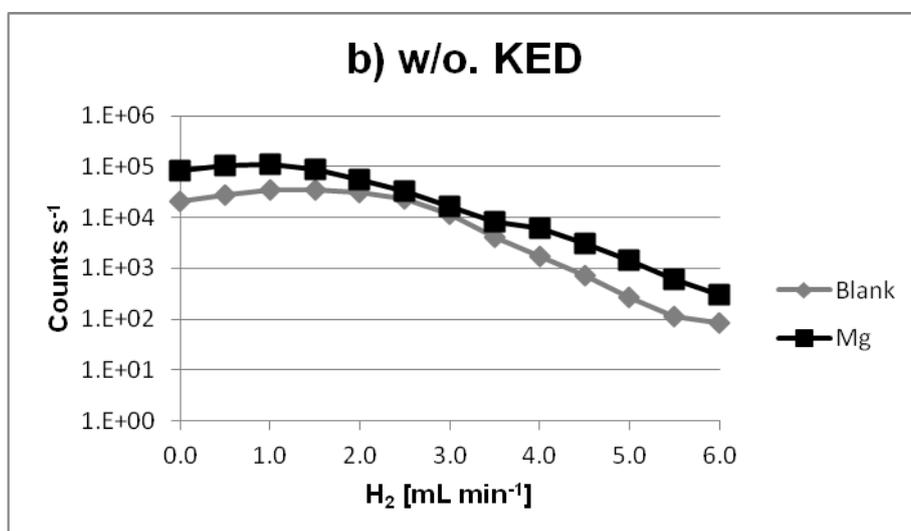
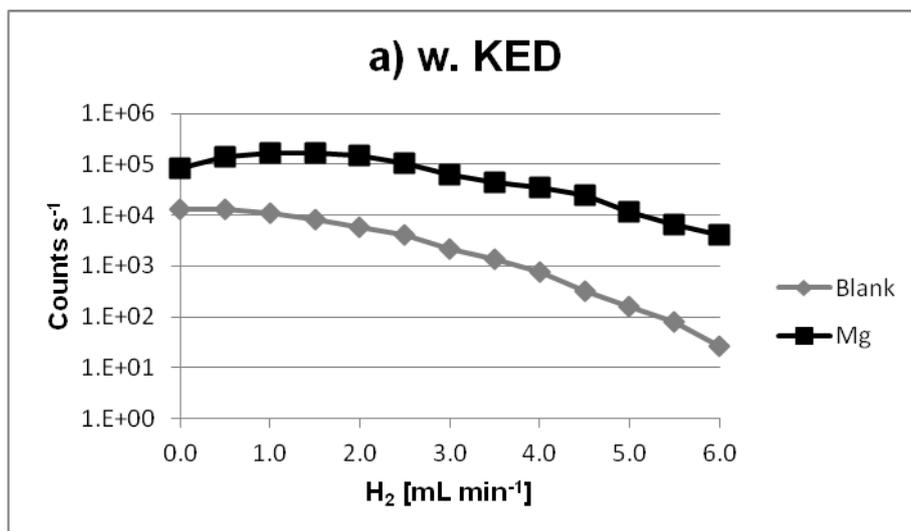


$^{137}\text{Ba}^+$

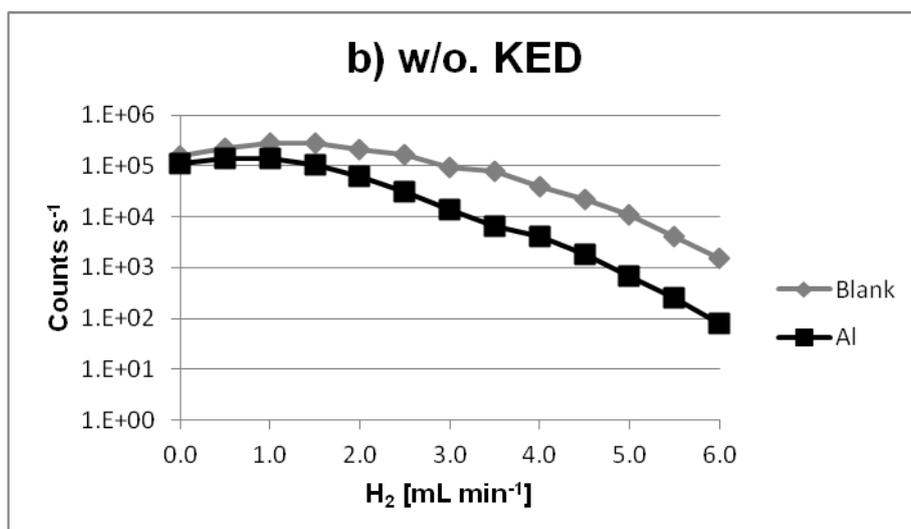
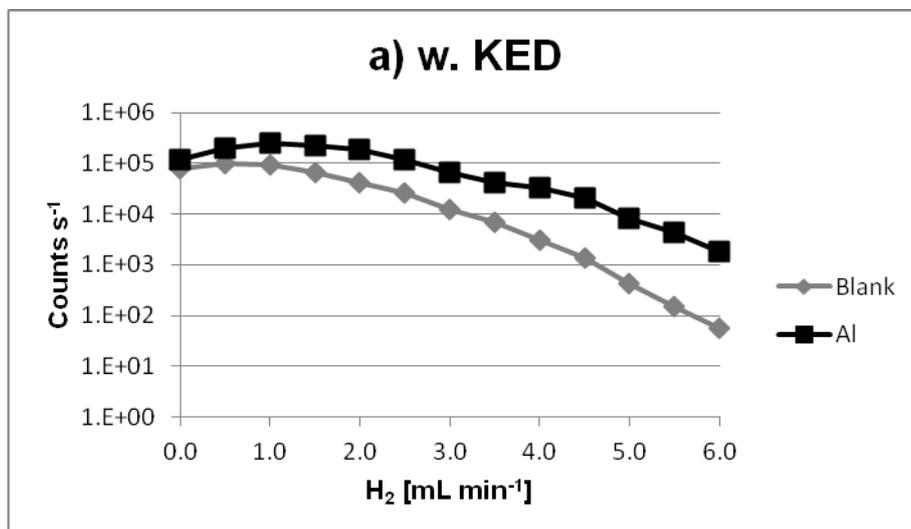


**Fig.S6.** Signal intensities of all elements and their interferences (blank) as a function of H<sub>2</sub> flow rate: a) w. KED and b) w/o. KED.

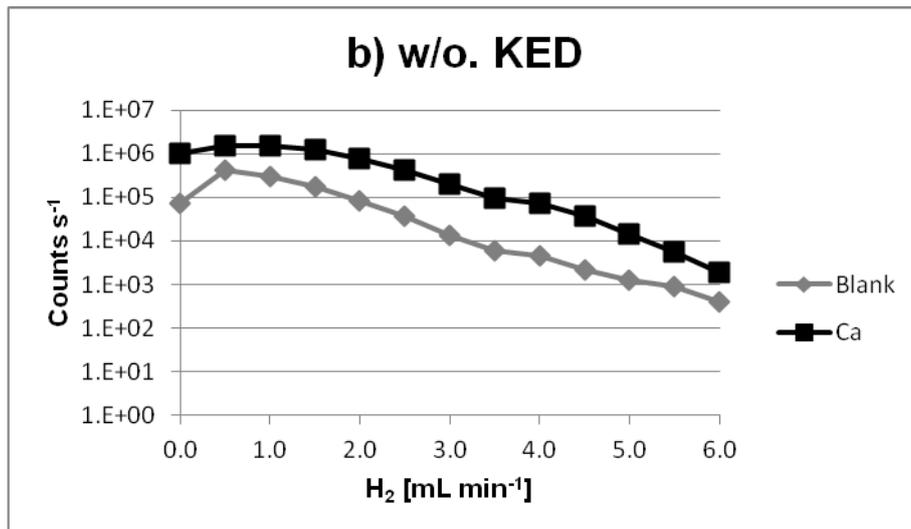
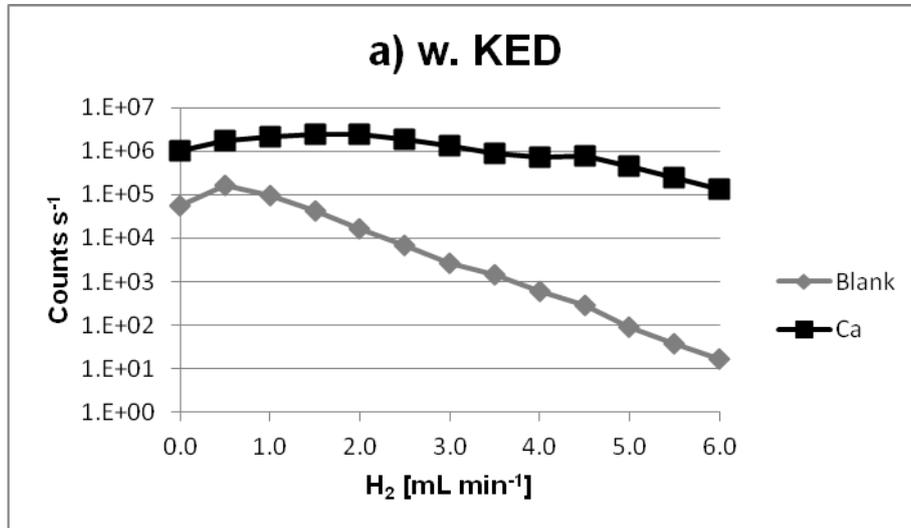
<sup>24</sup>Mg<sup>+</sup>



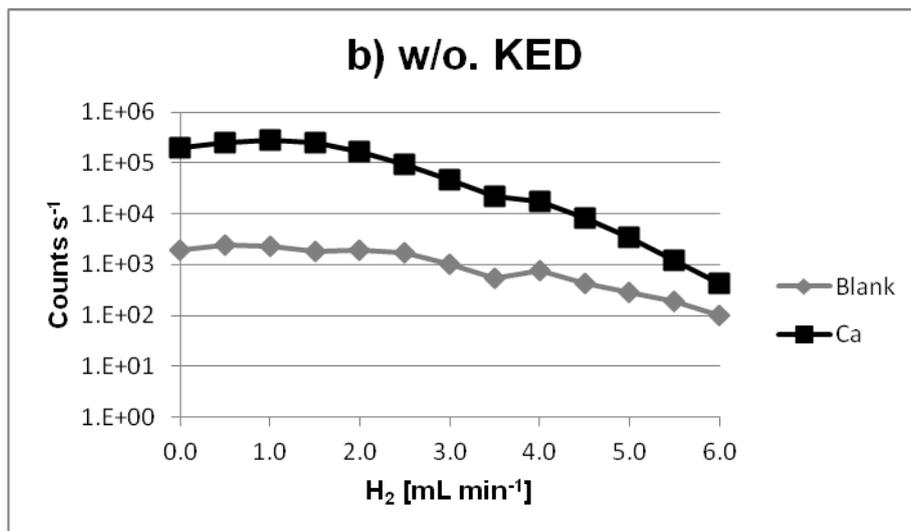
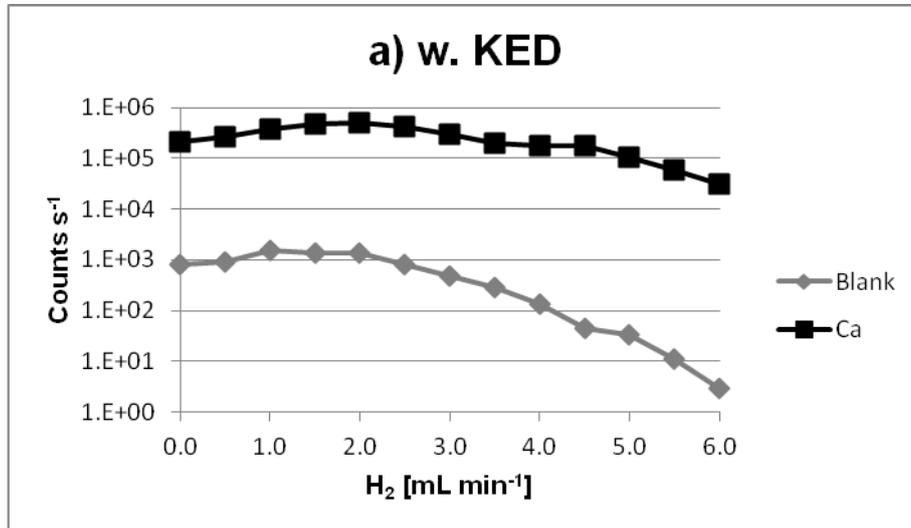
$^{27}\text{Al}^+$



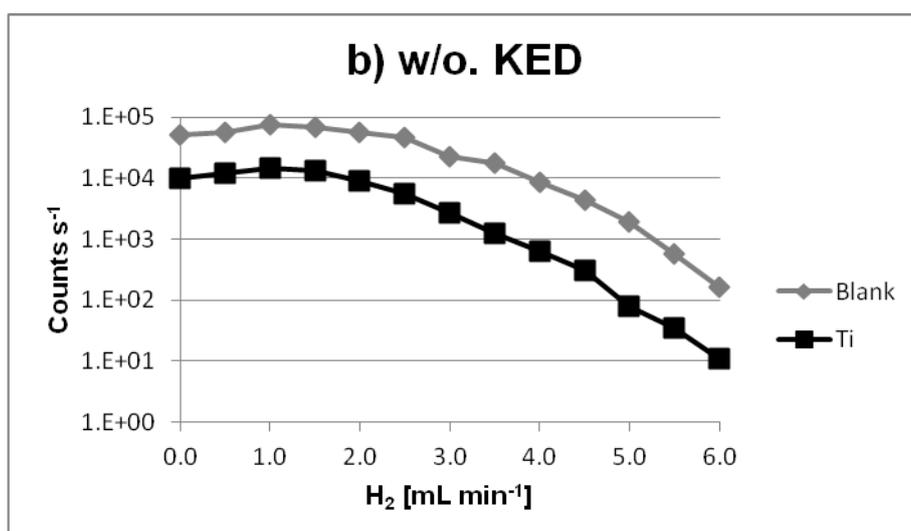
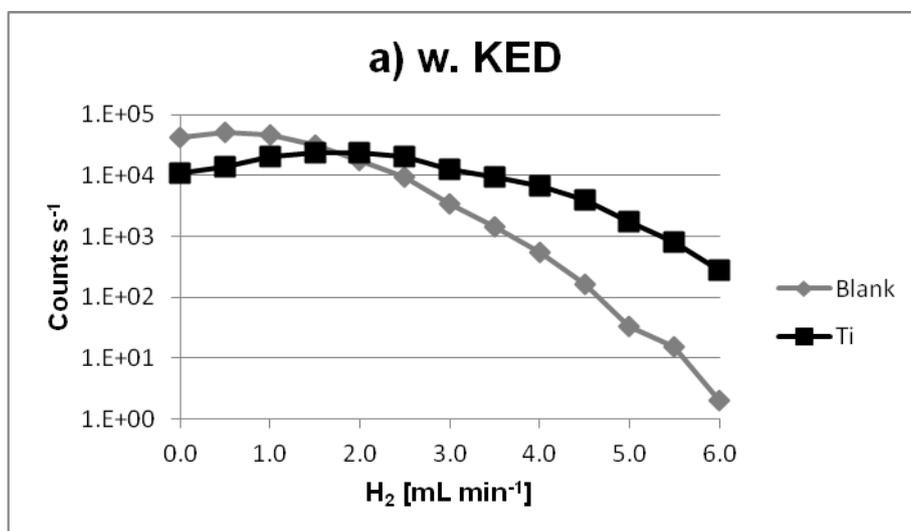
$^{42}\text{Ca}^+$



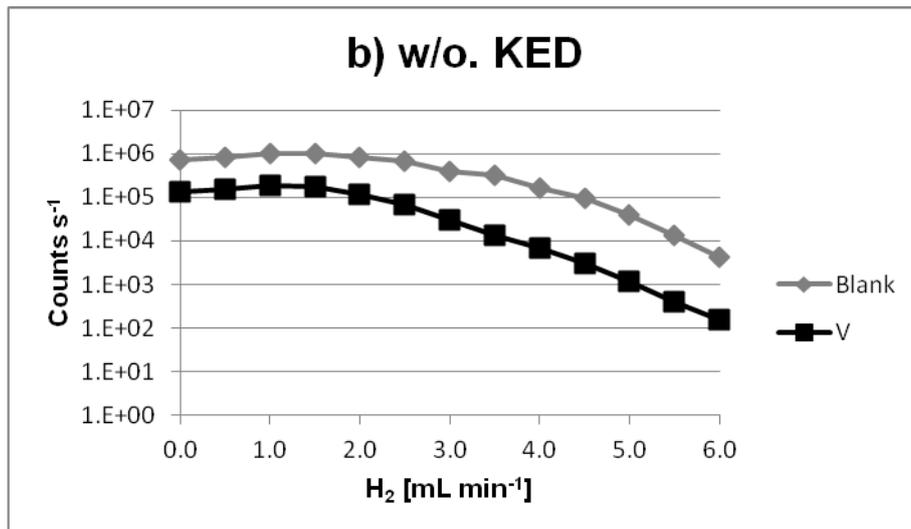
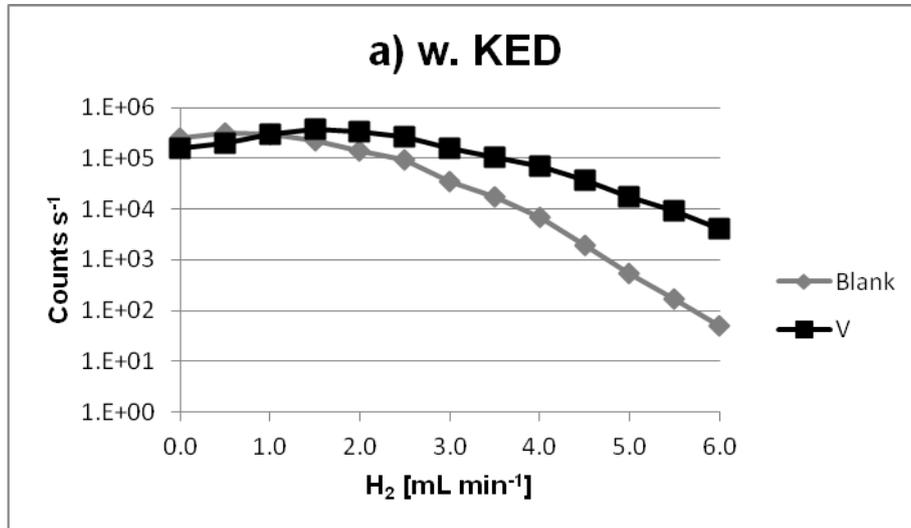
$^{43}\text{Ca}^+$

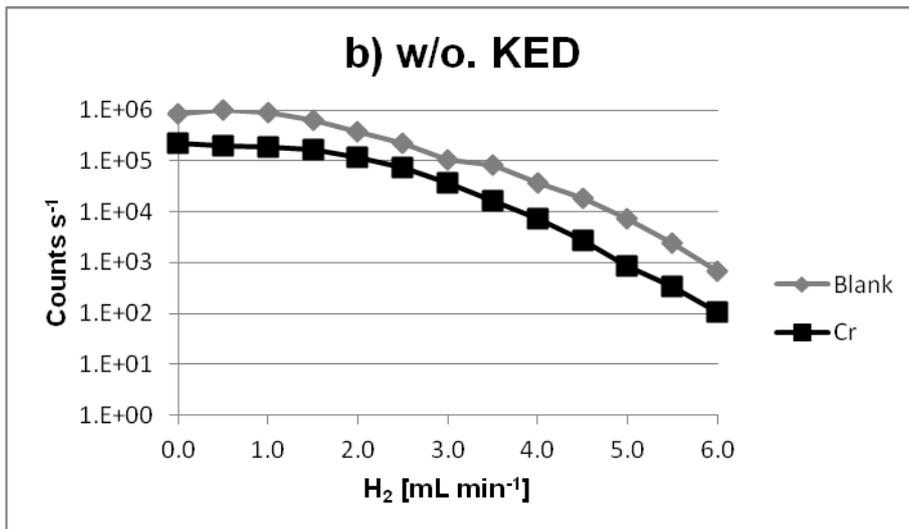
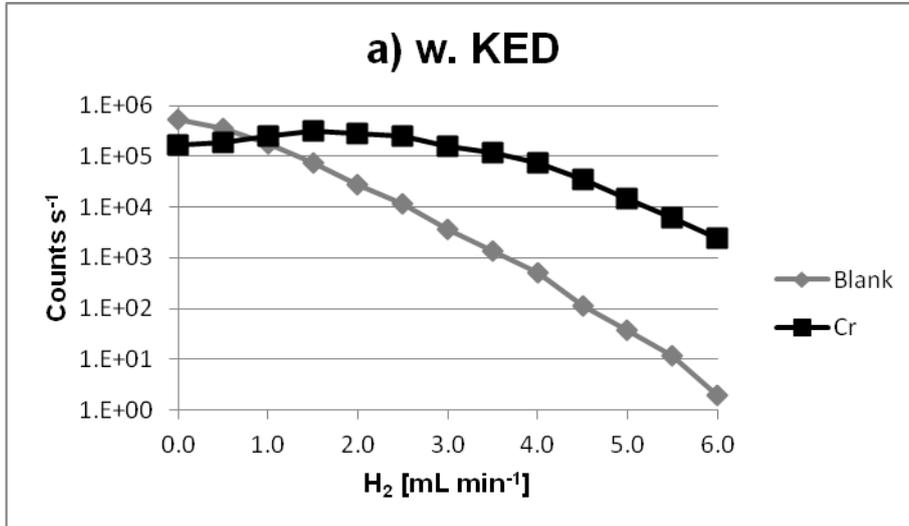


$^{47}\text{Ti}^+$

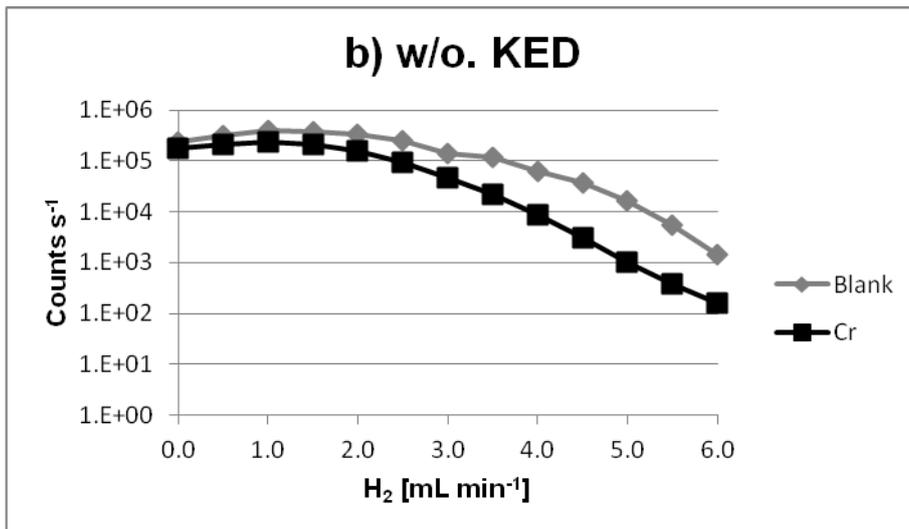
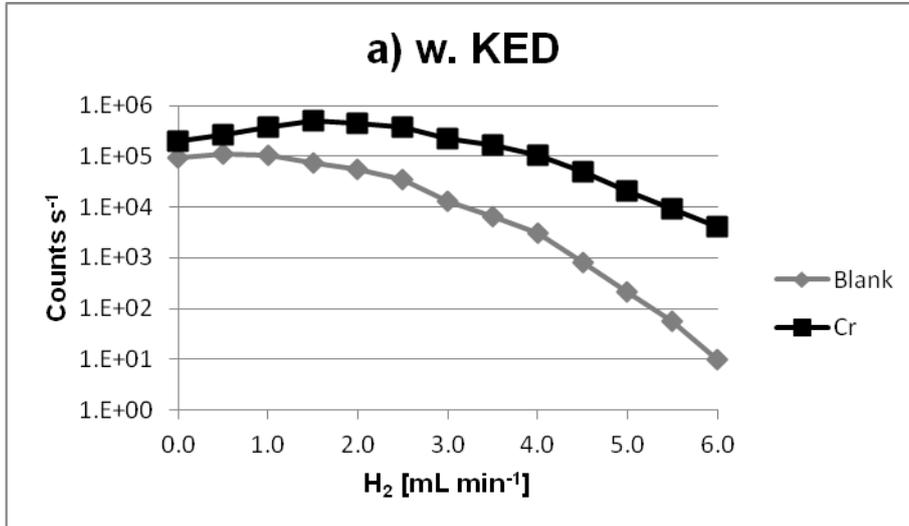


$^{51}\text{V}^+$

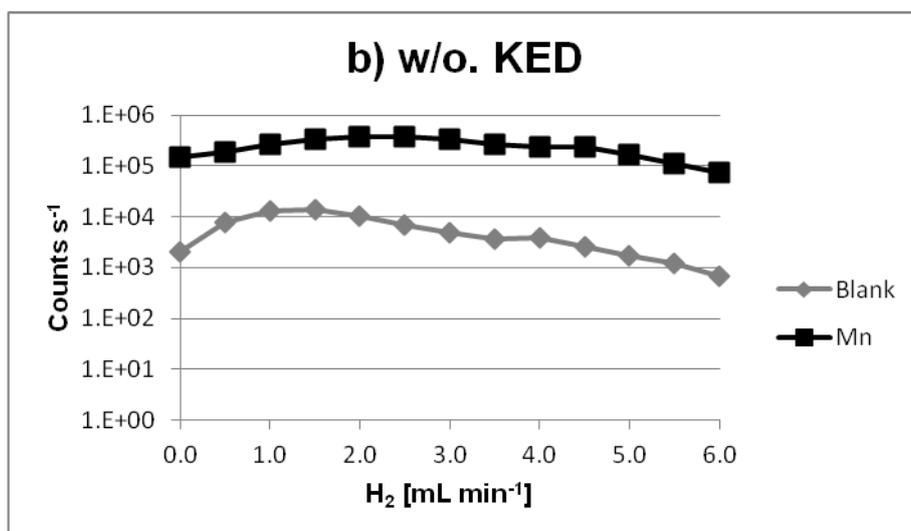
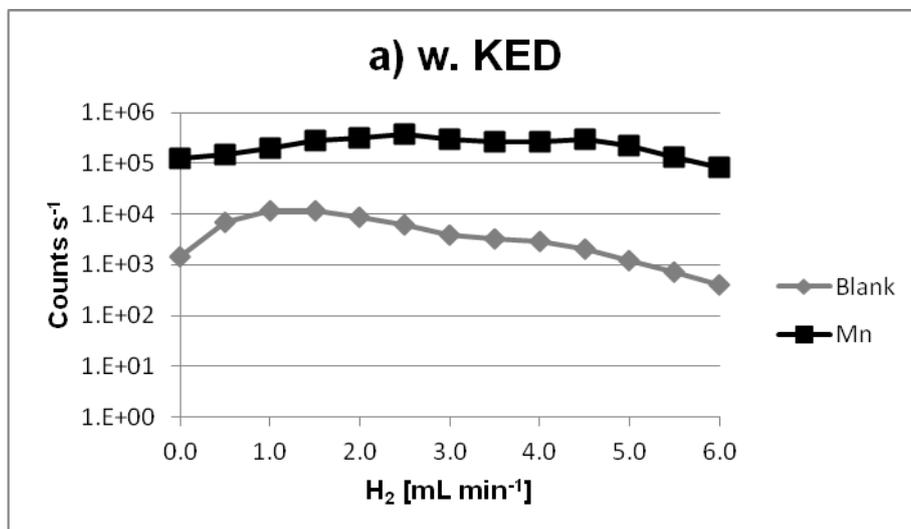




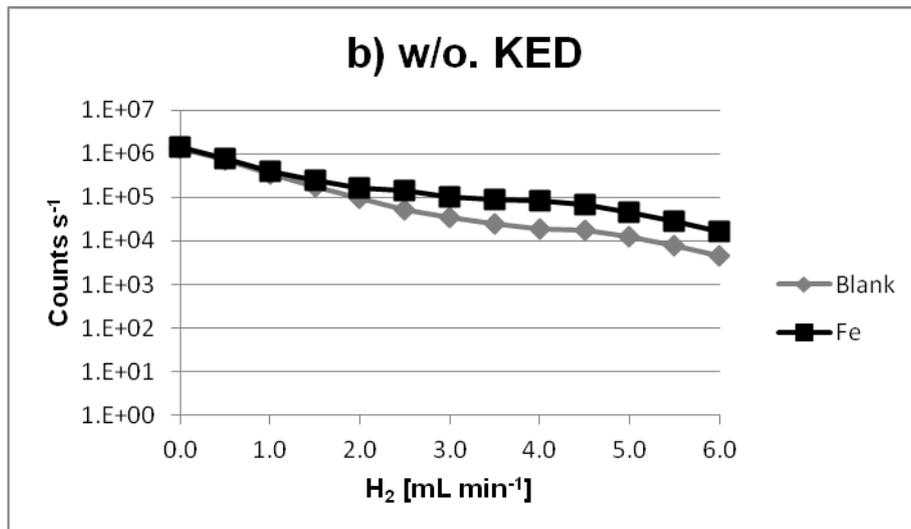
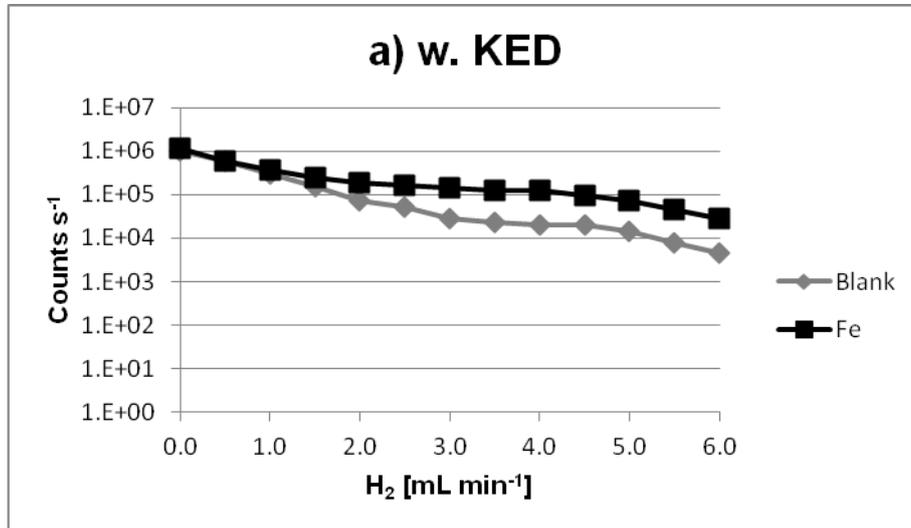
$^{53}\text{Cr}^+$



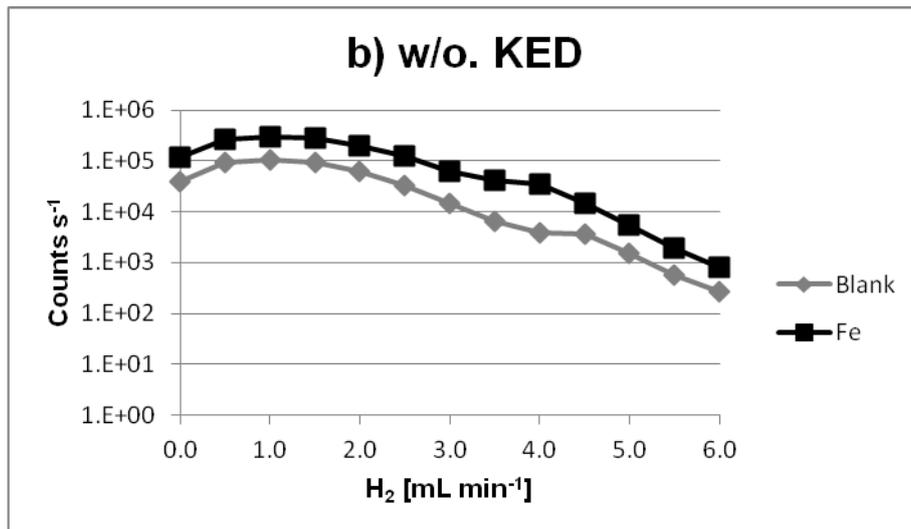
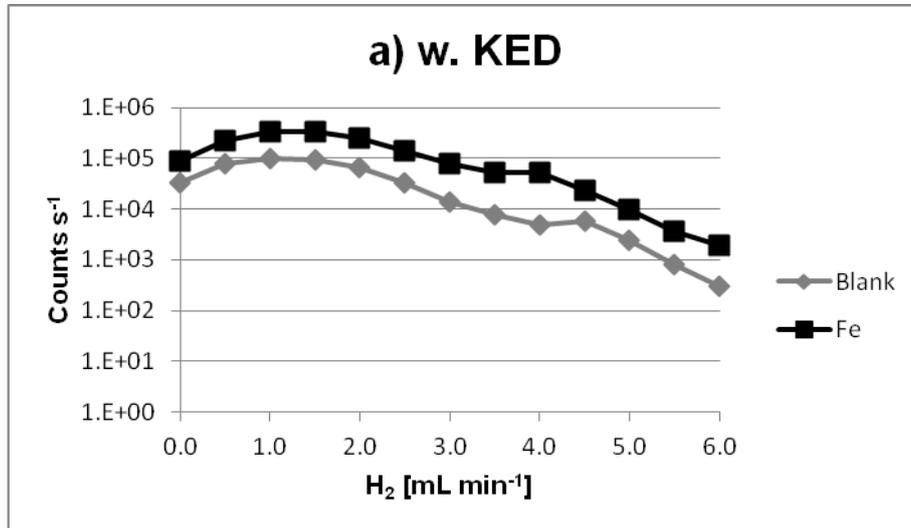
$^{55}\text{Mn}^+$



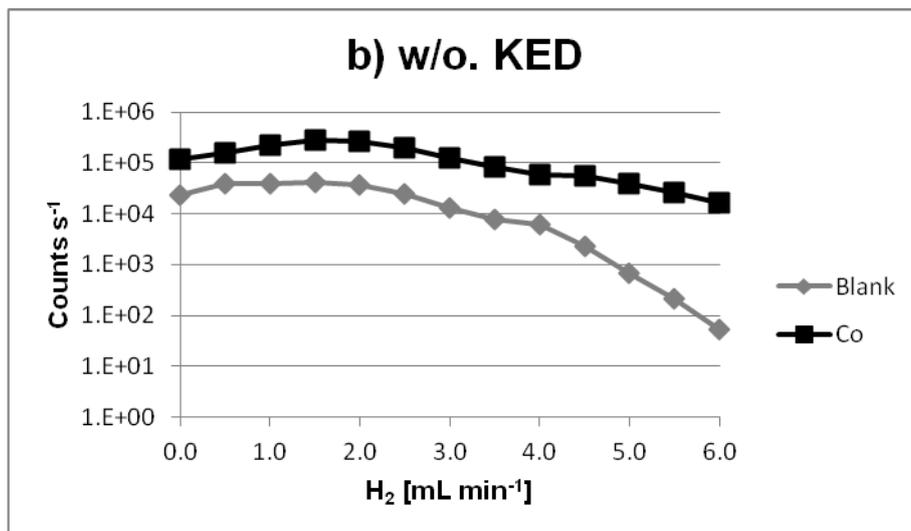
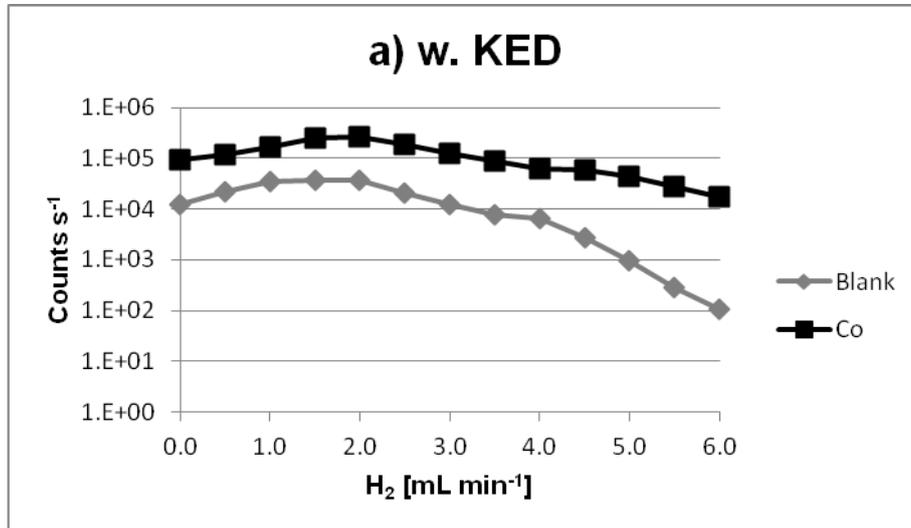
$^{56}\text{Fe}^+$



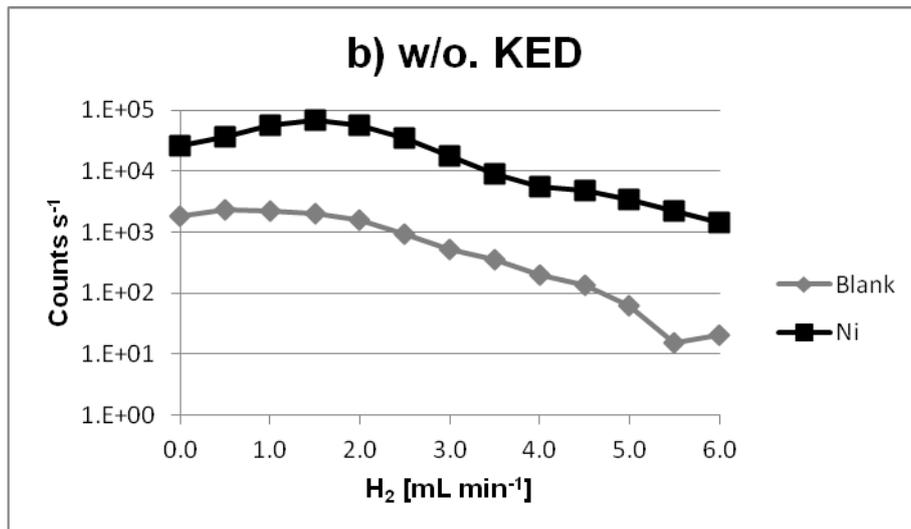
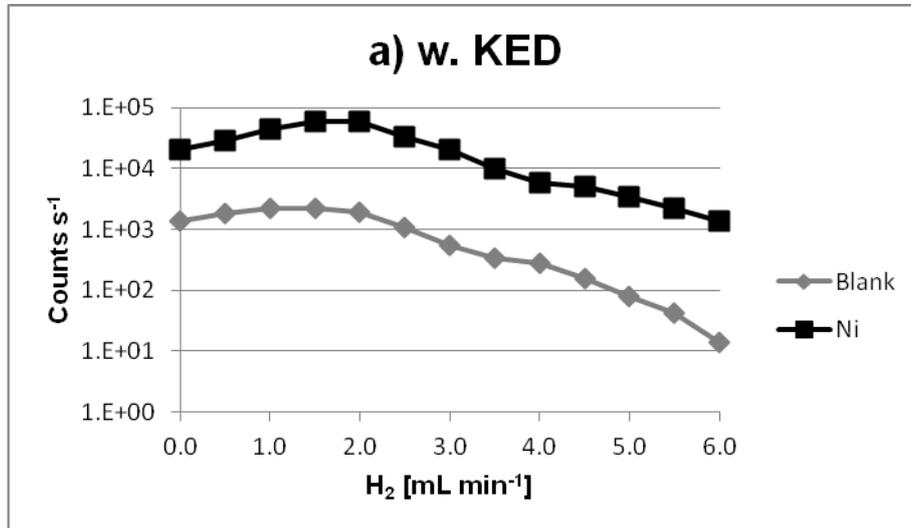
$^{57}\text{Fe}^+$



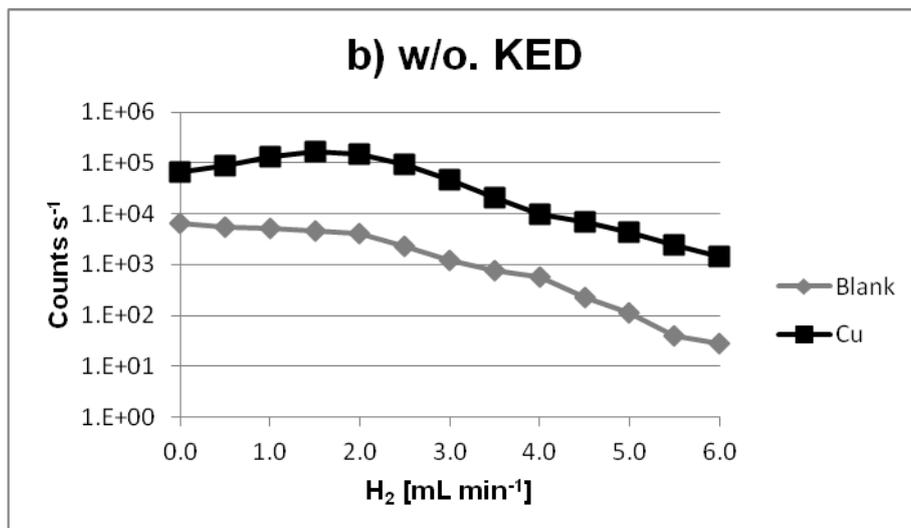
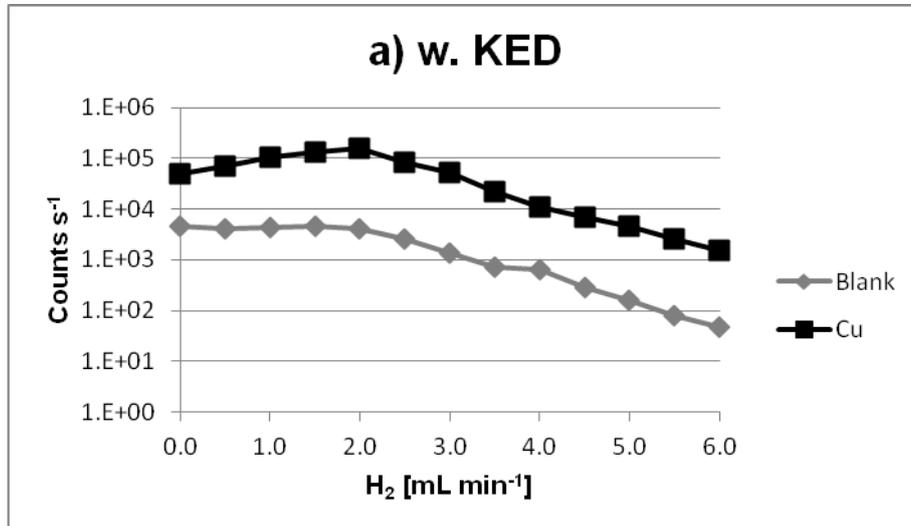
$^{59}\text{Co}^+$



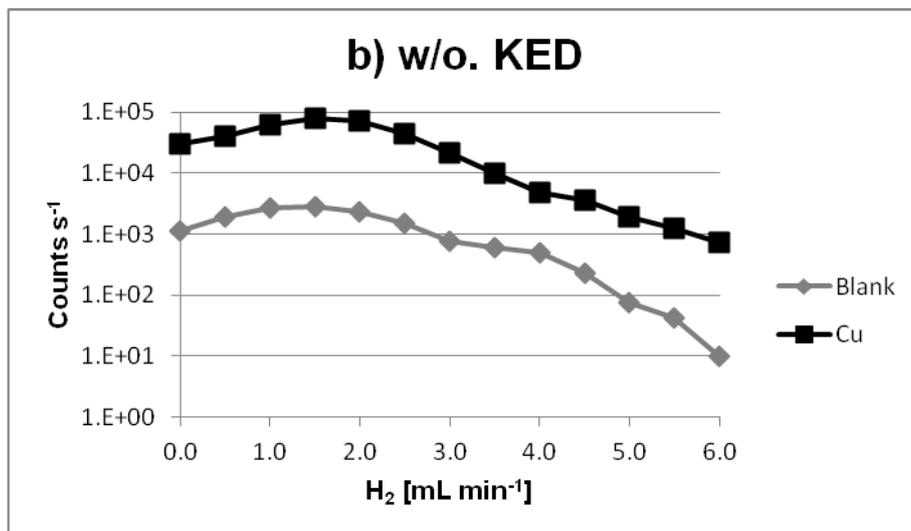
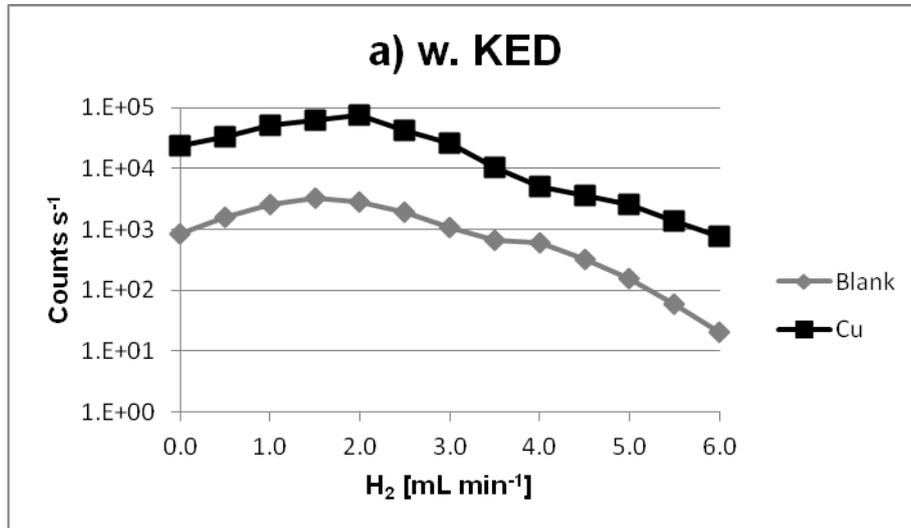
$^{60}\text{Ni}^+$



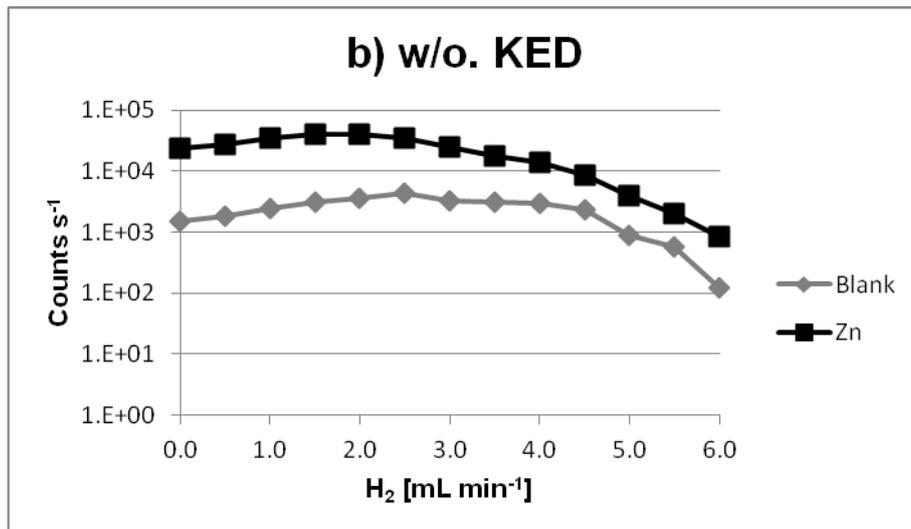
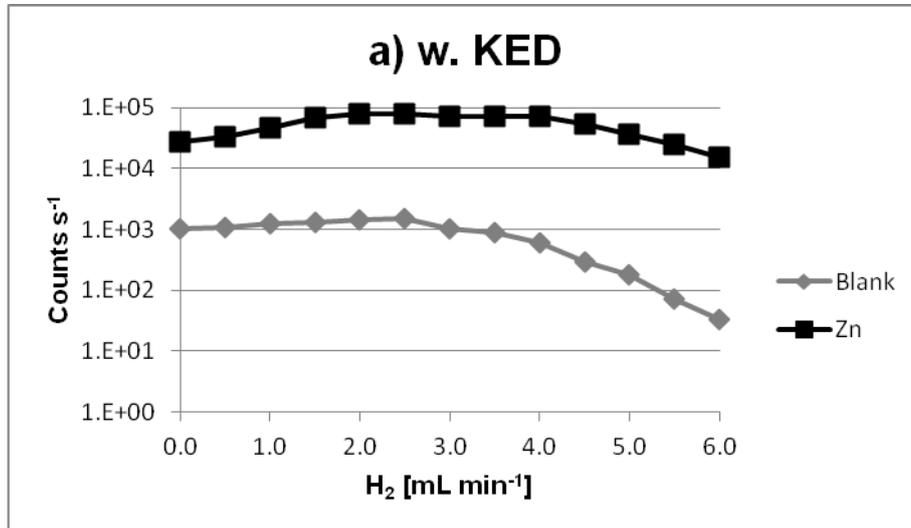
$^{63}\text{Cu}^+$



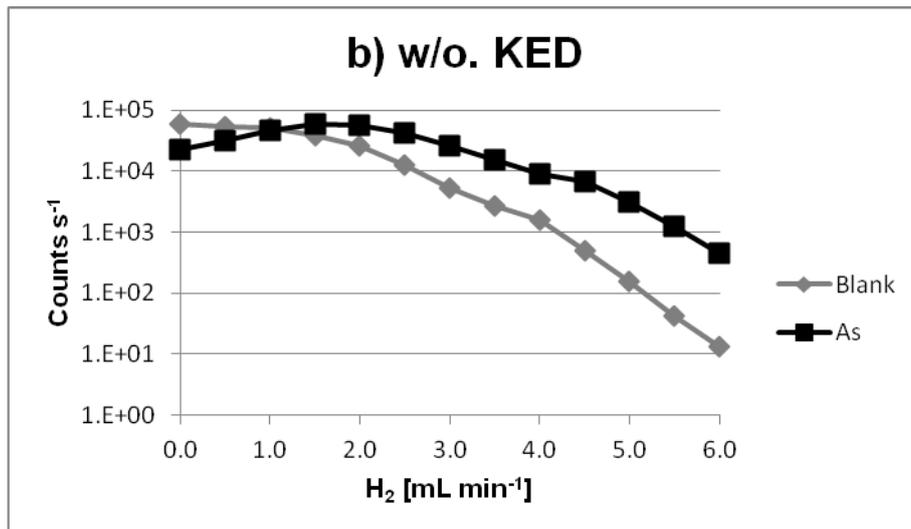
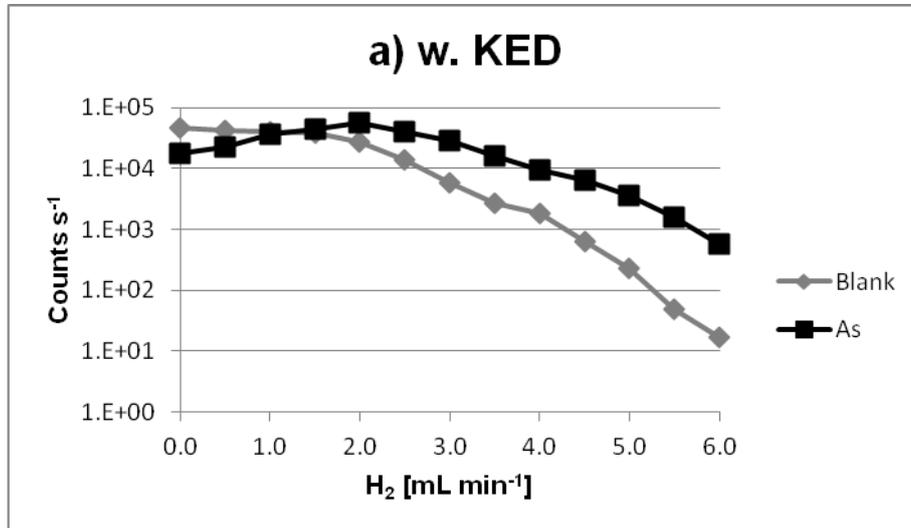
$^{65}\text{Cu}^+$



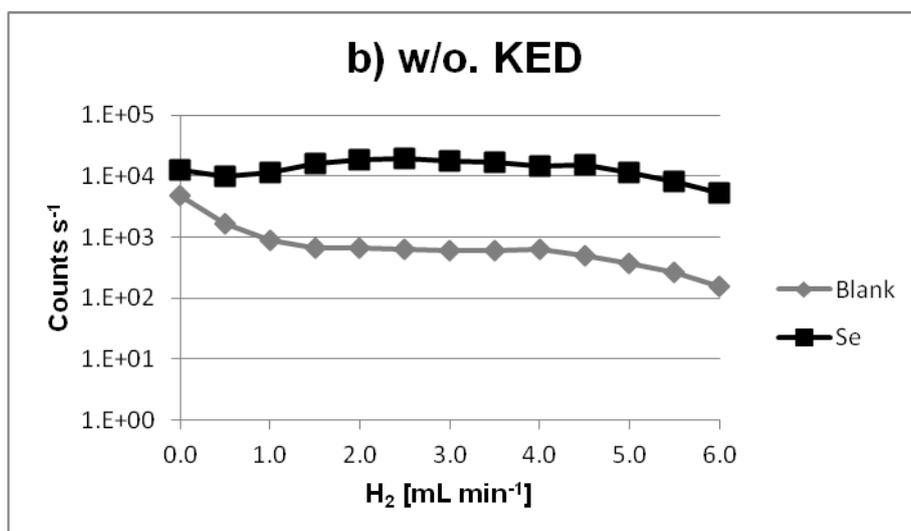
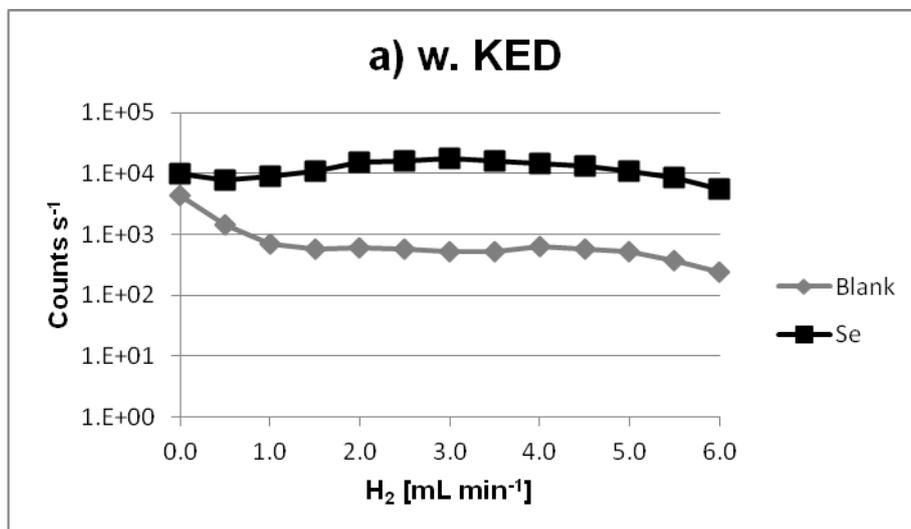
$^{66}\text{Zn}^+$



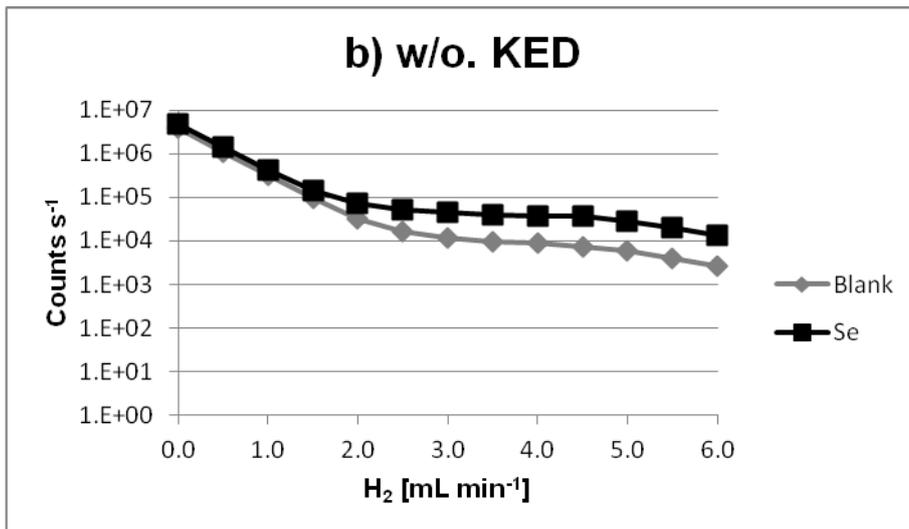
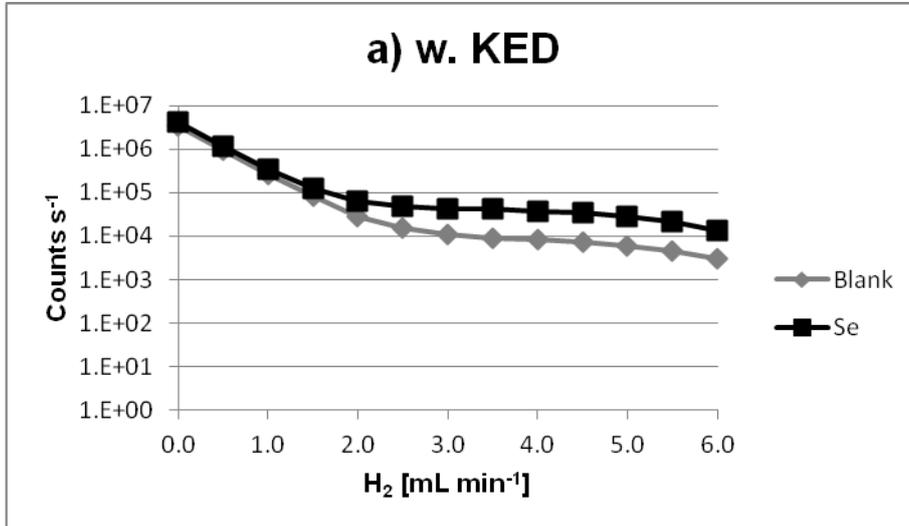
$^{75}\text{As}^+$



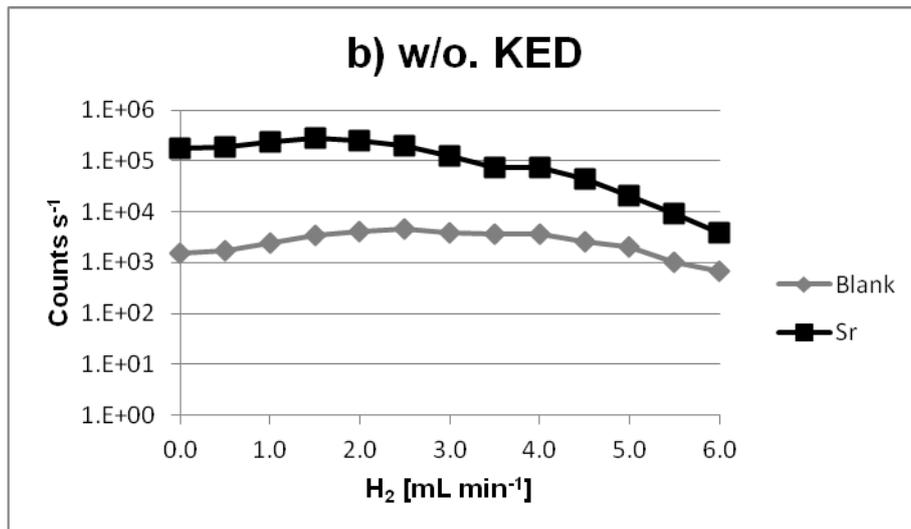
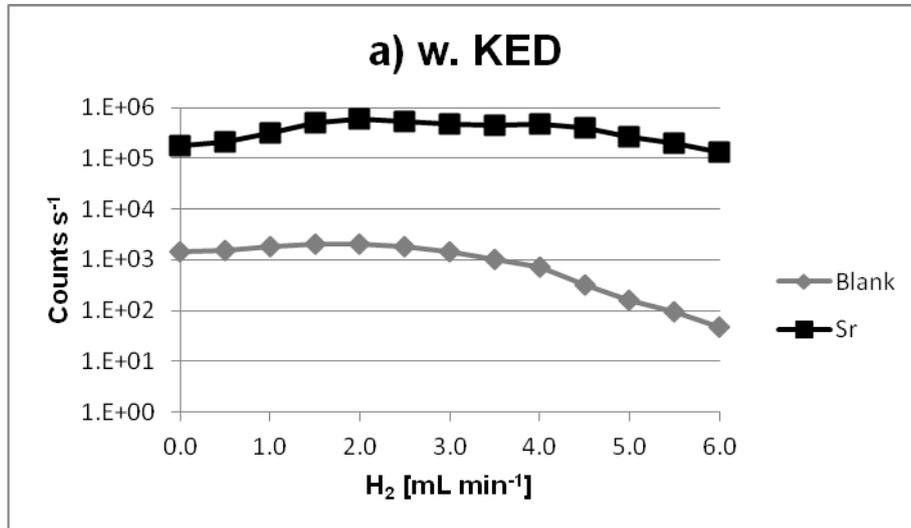
$^{78}\text{Se}^+$



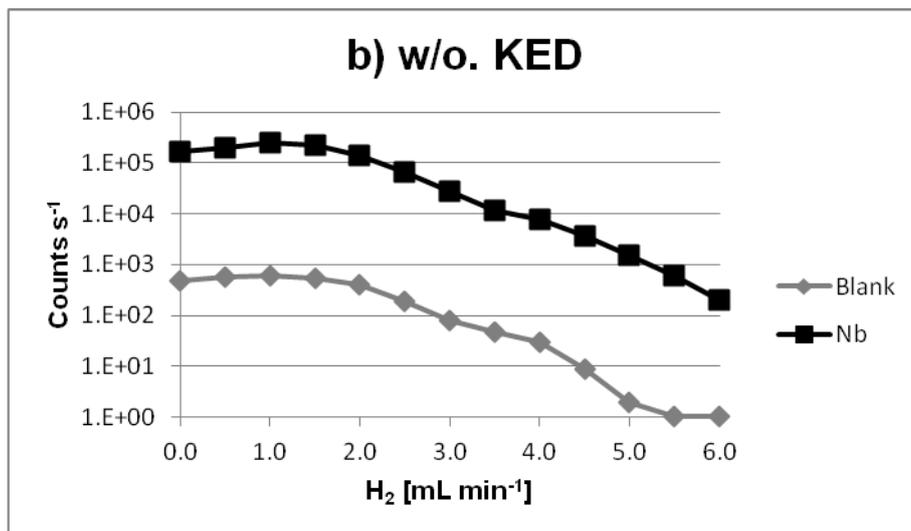
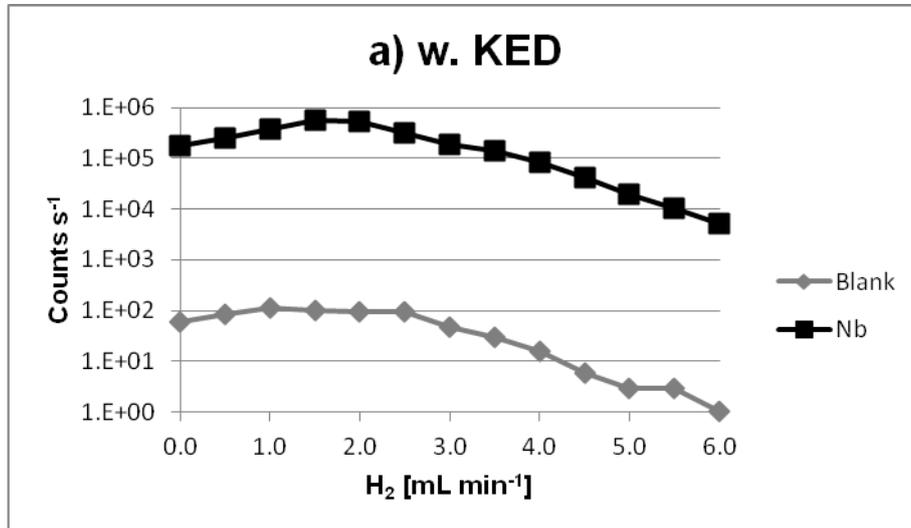
$^{80}\text{Se}^+$



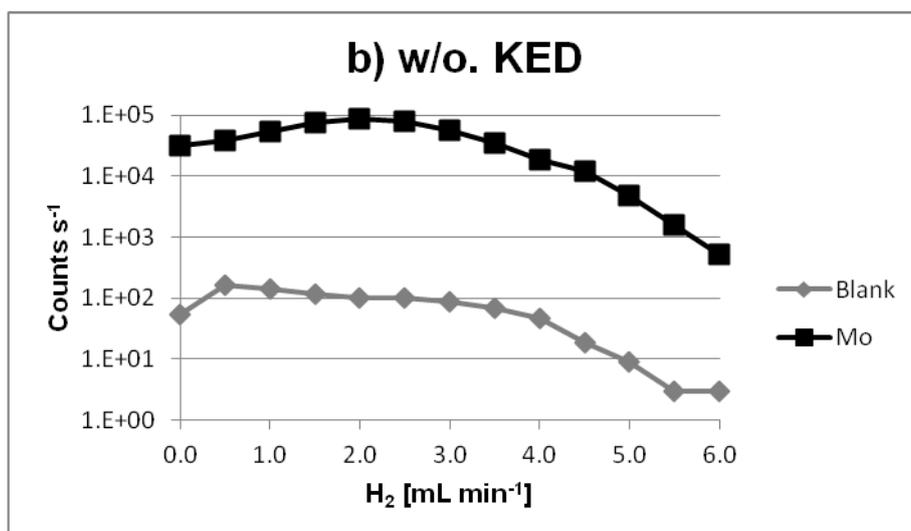
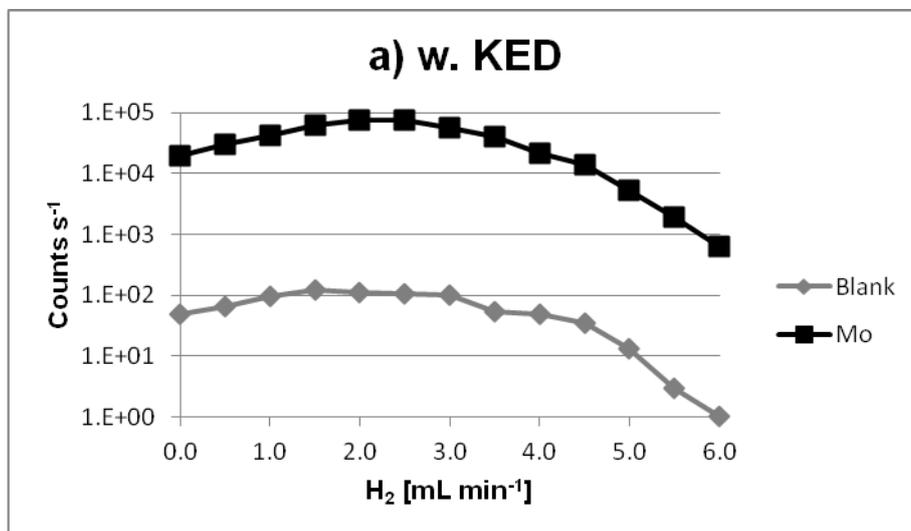
$^{88}\text{Sr}^+$



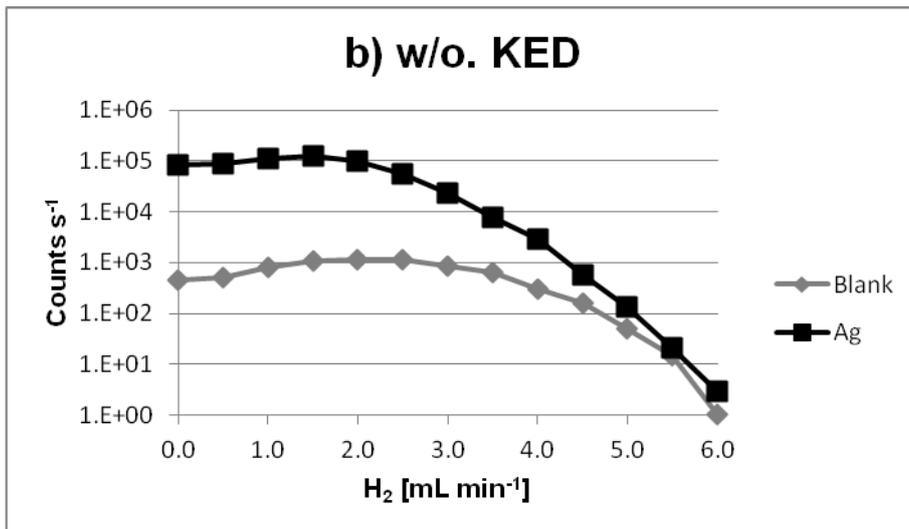
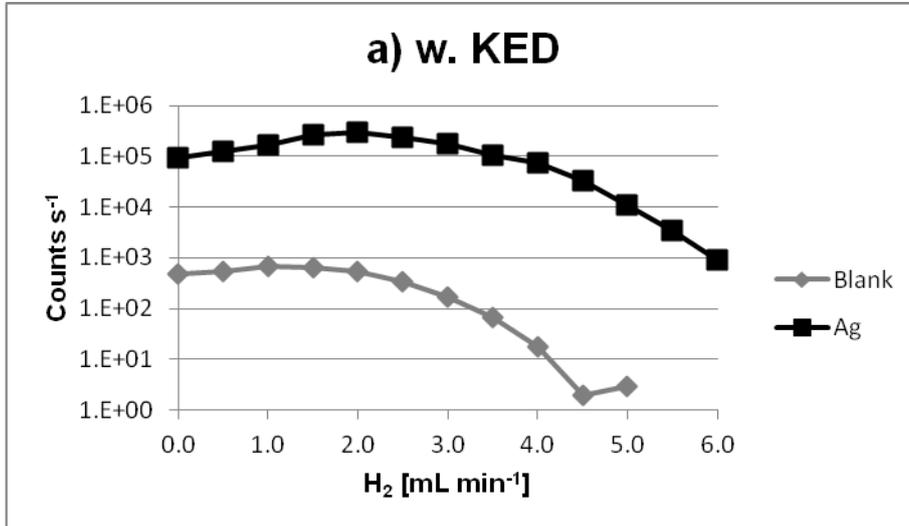
$^{93}\text{Nb}^+$



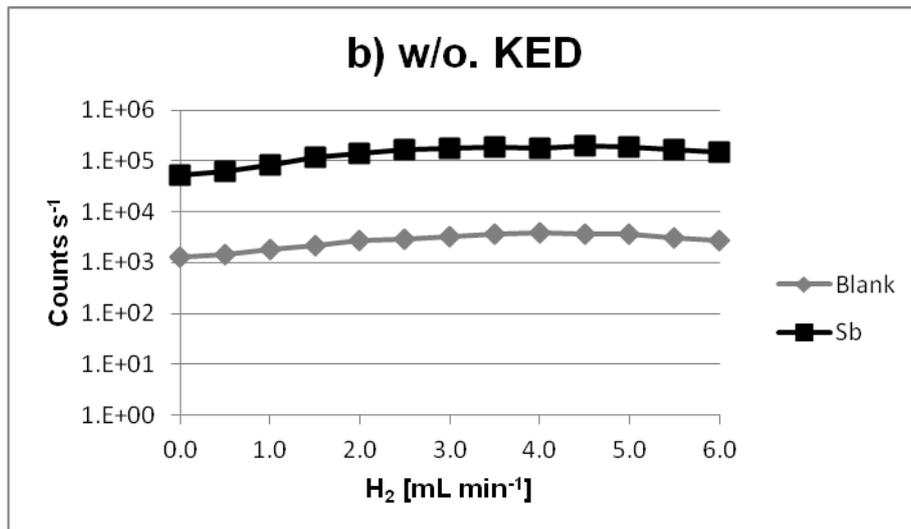
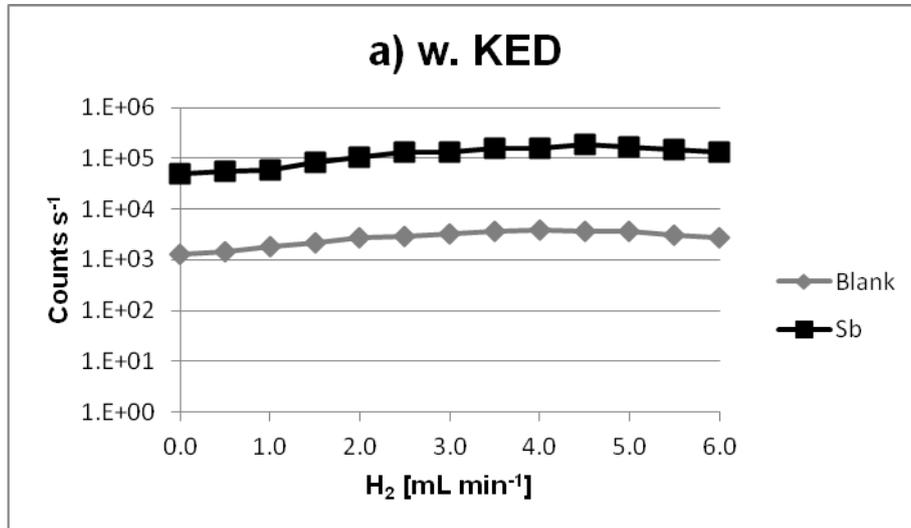
$^{95}\text{Mo}^+$



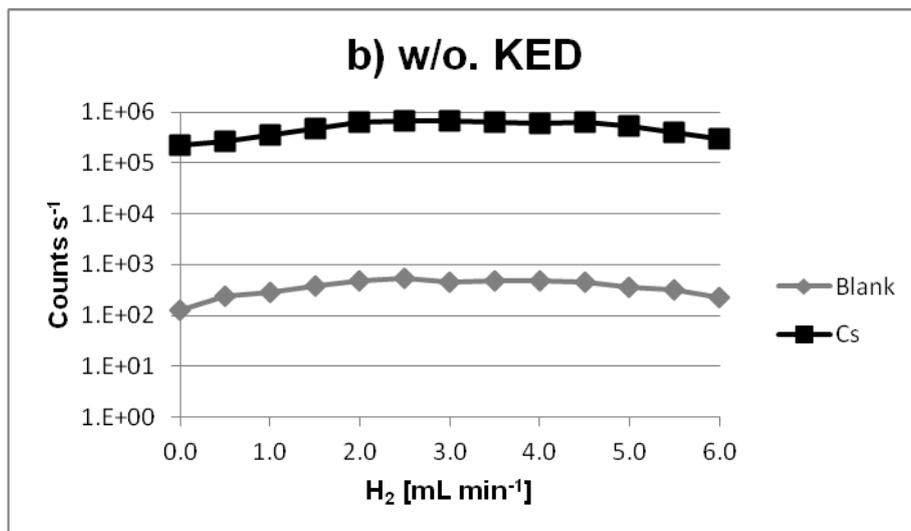
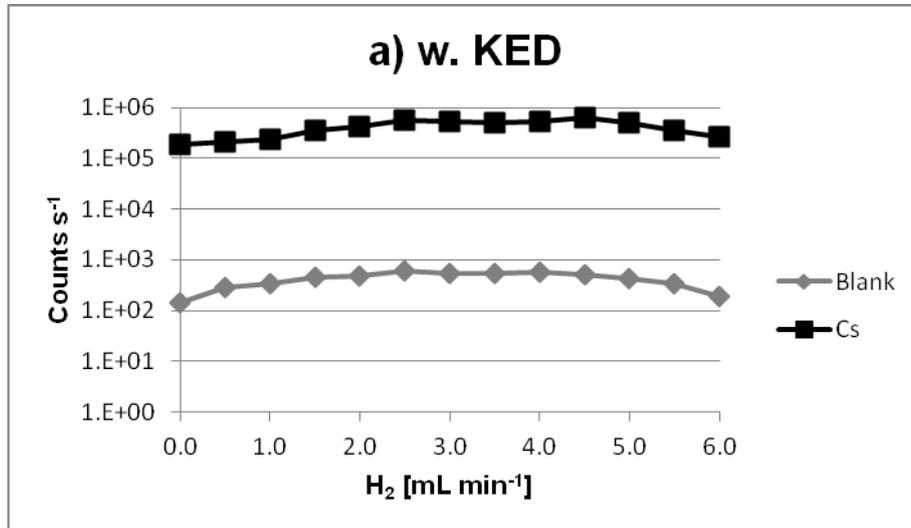
$^{107}\text{Ag}^+$



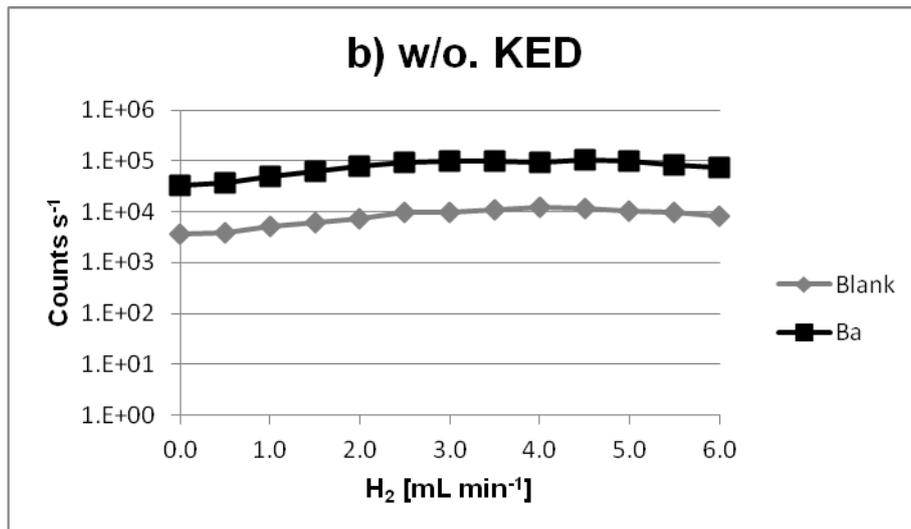
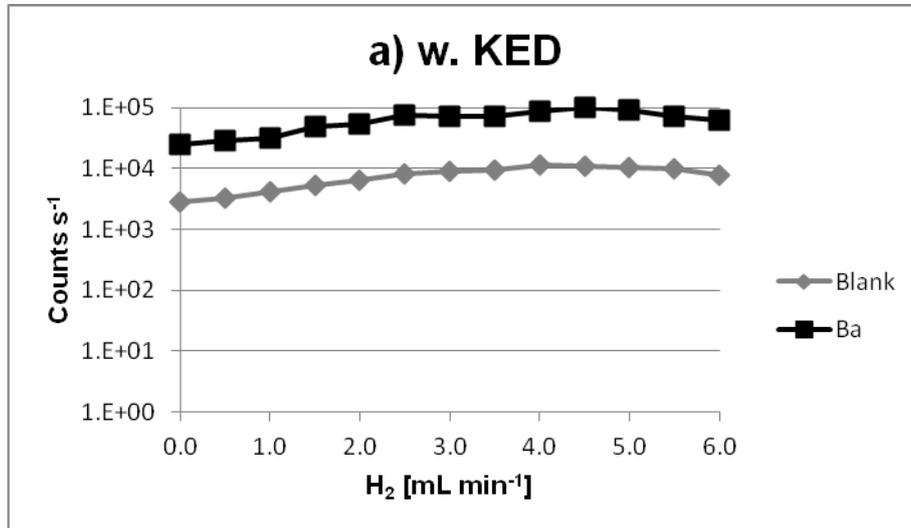
$^{121}\text{Sb}^+$



$^{133}\text{Cs}^+$



$^{137}\text{Ba}^+$



**Table S5** Stopping curves results of He gas flow rate

	2.5 mL min <sup>-1</sup> He				4.5 mL min <sup>-1</sup> He		
	E <sub>in</sub> (eV)	E <sub>loss</sub> (eV)	E <sub>out</sub> (eV)	$\sigma_X/\sigma_{Ni}$	E <sub>loss</sub> (eV)	E <sub>out</sub> (eV)	$\sigma_X/\sigma_{Ni}$
<sup>24</sup> Mg	21.0	8.8	12.2	0.50	11.9	9.1	0.48
m/z=24	20.8	9.1	11.8	0.98	10.5	10.3	0.38
<sup>27</sup> Al	21.1	8.9	12.2	0.56	11.3	9.8	0.49
m/z=27	20.7	8.7	12.0	0.42	11.6	9.1	0.50
<sup>39</sup> K	21.3	10.7	10.6	1.03	12.9	8.4	0.87
m/z=39	20.7	10.3	10.4	0.77	12.4	8.3	0.81
<sup>42</sup> Ca	21.4	10.2	11.2	1.03	12.9	8.5	0.93
m/z=42	20.8	10.4	10.4	0.84	13.2	7.6	0.96
<sup>43</sup> Ca	21.4	10.6	10.8	1.12	13.2	8.2	0.99
m/z=43	21.0	10.9	9.1	1.03	-	-	-
<sup>47</sup> Ti	21.5	9.8	11.7	1.09	13.0	8.5	1.04
m/z=47	20.9	11.5	9.4	1.08	13.9	7.0	1.16
<sup>51</sup> V	21.6	9.4	12.2	1.11	11.5	10.1	0.93
m/z=51	20.9	11.8	9.1	1.22	13.0	7.9	1.12
<sup>52</sup> Cr	21.6	8.9	12.7	1.05	11.6	10.0	0.96
m/z=52	21.0	9.2	11.8	0.86	12.5	8.5	1.06
<sup>53</sup> Cr	21.7	9.4	12.3	1.13	12.5	9.2	1.01
m/z=53	21.0	11.2	9.8	1.26	13.8	7.2	1.25
<sup>55</sup> Mn	21.6	9.7	11.9	1.25	12.6	9.0	1.15
m/z=55	21.0	9.8	11.2	0.99	12.8	8.2	1.17
<sup>56</sup> Fe	21.4	11.4	10.0	1.62	11.9	9.5	1.09
m/z=56	21.1	10.4	10.7	1.09	11.6	9.5	1.01
<sup>57</sup> Fe	21.2	12.2	9.0	1.86	12.2	9.0	1.17
m/z=57	20.9	10.9	10.0	1.21	10.9	10.0	0.95
<sup>59</sup> Co	21.7	8.2	13.5	1.06	11.3	10.4	1.04
m/z=59	20.9	11.8	9.1	1.41	12.7	8.2	1.25
<sup>60</sup> Ni	21.7	7.7	14.0	1	10.9	10.8	1
m/z=60	20.9	9.2	11.7	1	10.9	10.0	1
<sup>63</sup> Cu	21.8	7.8	14.0	1.06	10.4	11.4	0.98
m/z=63	21.3	8.3	13.0	0.89	10.3	11.0	0.94
<sup>65</sup> Cu	21.9	7.9	14.0	1.11	10.9	11.0	1.07
m/z=65	21.0	7.8	13.2	0.87	10.6	10.4	1.03
<sup>66</sup> Zn	22.0	9.1	12.9	1.34	12.3	9.7	1.29
m/z=66	21.1	9.0	12.1	1.05	12.3	8.8	1.31
<sup>75</sup> As	21.9	9.9	12.0	1.72	12.9	9.0	1.59
m/z=75	21.3	12.5	8.8	1.90	14.3	7.0	1.89
<sup>78</sup> Se	21.9	11.4	10.5	2.18	14.1	7.8	1.92
m/z=78	21.3	12.5	8.8	1.98	-	-	-

*(continued)*

(continued)

	2.5 mL min <sup>-1</sup> He				4.5 mL min <sup>-1</sup> He		
	E <sub>in</sub> (eV)	E <sub>loss</sub> (eV)	E <sub>out</sub> (eV)	σ <sub>X</sub> /σ <sub>Ni</sub>	E <sub>loss</sub> (eV)	E <sub>out</sub> (eV)	σ <sub>X</sub> /σ <sub>Ni</sub>
<sup>88</sup> Sr	22.2	11.4	10.8	2.41	14.7	7.5	2.28
m/z=88	21.9	11.1	10.8	1.79	14.7	7.2	2.21
<sup>93</sup> Nb	22.4	9.8	12.6	2.03	12.9	9.5	1.91
m/z=93	21.3	9.2	12.1	1.51	12.4	8.9	1.84
<sup>95</sup> Mo	22.3	9.2	13.1	1.92	12.3	10.0	1.82
m/z=95	22.2	12.4	9.8	2.23	13.7	8.5	2.06
<sup>107</sup> Ag	22.4	8.7	13.7	2.00	12.2	10.2	2.01
m/z=107	22.1	9.0	13.1	1.61	12.3	9.8	1.97
<sup>121</sup> Sb	22.8	10.8	12.0	2.95	14.8	8.0	3.03
m/z=121	22.2	11.3	10.9	2.47	14.6	7.6	2.93
<sup>133</sup> Cs	22.8	11.8	11.0	3.69	15.6	7.2	3.66
m/z=133	22.6	12.4	10.2	3.04	17.8	4.8	4.70
<sup>137</sup> Ba	22.9	11.2	11.7	3.50	15.1	7.8	3.52
m/z=137	22.7	11.5	11.2	2.78	15.3	7.4	3.47

**Table S6** Stopping curves results of H<sub>2</sub> gas flow rate

	2.5 mL min <sup>-1</sup> H <sub>2</sub>				4.5 mL min <sup>-1</sup> H <sub>2</sub>		
	E <sub>in</sub> (eV)	E <sub>loss</sub> (eV)	E <sub>out</sub> (eV)	σ <sub>X</sub> /σ <sub>Ni</sub>	E <sub>loss</sub> (eV)	E <sub>out</sub> (eV)	σ <sub>X</sub> /σ <sub>Ni</sub>
<sup>24</sup> Mg	21.0	9.9	11.1	0.36	12.7	8.3	0.45
m/z=24	20.8	10.8	10.0	0.40	12.8	8.0	0.37
<sup>27</sup> Al	21.1	10.3	10.8	0.43	13.1	8.0	0.53
m/z=27	20.7	10.2	10.5	0.42	13.2	7.5	0.44
<sup>42</sup> Ca	21.4	10.4	11.0	0.66	13.3	8.1	0.82
m/z=42	20.8	10.3	10.5	0.66	13.3	7.5	0.69
<sup>43</sup> Ca	21.4	10.4	11.0	0.67	13.3	8.1	0.84
m/z=43	21.0	10.5	10.5	0.68	13.2	7.8	0.68
<sup>47</sup> Ti	21.5	9.8	11.7	0.67	12.9	8.6	0.87
m/z=47	20.9	11.1	9.8	0.82	13.6	7.3	0.79
<sup>51</sup> V	21.6	10.4	11.2	0.79	13.6	8.0	1.02
m/z=51	20.9	10.9	10.0	0.86	14.2	6.7	0.93
<sup>52</sup> Cr	21.6	9.6	12.0	0.72	13.4	8.2	1.02
m/z=52	21.0	11.7	9.3	0.97	14.8	6.2	1.02
<sup>53</sup> Cr	21.7	9.5	12.2	0.72	13.7	8.0	1.07
m/z=53	21.0	11.0	10.0	0.90	14.4	6.6	0.98
<sup>55</sup> Mn	21.6	8.4	13.2	0.64	12.0	9.6	0.90
m/z=55	21.0	10.5	10.5	0.87	12.0	9.0	0.75
<sup>56</sup> Fe	21.4	8.5	12.9	0.67	11.9	9.5	0.92
m/z=56	21.1	8.8	12.3	0.69	11.1	10.0	0.67
<sup>57</sup> Fe	21.2	12.4	8.8	1.18	15.2	6.0	1.45
m/z=57	20.9	12.4	8.5	1.18	15.2	5.7	1.19
<sup>59</sup> Co	21.7	9.8	11.9	0.84	12.1	9.6	0.97
m/z=59	20.9	11.3	9.6	1.05	14.5	6.4	1.12
<sup>60</sup> Ni	21.7	11.0	10.7	1	12.2	9.5	1
m/z=60	20.9	10.8	10.1	1	13.5	7.4	1
<sup>63</sup> Cu	21.8	11.3	10.5	1.08	13.5	8.3	1.23
m/z=63	21.3	11.3	10.0	1.09	14.5	6.8	1.15
<sup>65</sup> Cu	21.9	11.5	10.4	1.14	13.9	8.0	1.32
m/z=65	21.0	11.6	9.4	1.20	14.6	6.4	1.24
<sup>66</sup> Zn	22.0	8.4	13.6	0.75	12.0	10.0	1.05
m/z=66	21.1	8.0	13.1	0.72	11.7	9.4	0.86
<sup>75</sup> As	21.9	11.1	10.8	1.25	14.8	6.1	1.93
m/z=75	21.3	11.9	9.4	1.41	15.3	6.0	1.53
<sup>78</sup> Se	21.9	8.0	13.9	0.84	12.2	9.7	1.28
m/z=78	21.3	8.3	13.0	0.88	12.4	8.9	1.09
<sup>88</sup> Sr	22.2	9.2	13.0	1.11	12.6	9.6	1.49
m/z=88	21.9	9.7	12.3	1.16	12.9	9.0	1.26

*(continued)*

(continued)

	2.5 mL min <sup>-1</sup> H <sub>2</sub>				4.5 mL min <sup>-1</sup> H <sub>2</sub>		
	E <sub>in</sub> (eV)	E <sub>loss</sub> (eV)	E <sub>out</sub> (eV)	σ <sub>X</sub> /σ <sub>Ni</sub>	E <sub>loss</sub> (eV)	E <sub>out</sub> (eV)	σ <sub>X</sub> /σ <sub>Ni</sub>
<sup>93</sup> Nb	22.4	11.9	10.5	1.66	14.7	7.7	2.00
m/z=93	21.3	11.1	10.2	1.57	15.3	6.0	1.89
<sup>95</sup> Mo	22.3	10.7	11.6	1.46	15.7	6.6	2.33
m/z=95	22.2	11.2	11.0	1.53	15.5	6.7	1.83
<sup>107</sup> Ag	22.4	10.9	11.5	1.68	15.9	6.5	2.67
m/z=107	22.1	11.1	11.0	1.71	15.8	6.3	2.16
<sup>121</sup> Sb	22.8	6.8	16.0	1.01	10.6	12.2	1.53
m/z=121	22.2	7.3	14.9	1.11	10.5	11.7	1.24
<sup>133</sup> Cs	22.8	8.9	13.9	1.55	13.1	9.7	2.29
m/z=133	22.6	10.4	12.2	1.88	13.6	9.0	1.97
<sup>137</sup> Ba	22.9	8.7	14.2	1.54	11.9	11.0	2.03
m/z=137	22.7	9.0	13.7	1.59	13.3	9.4	1.94