Application of Delay Before Burst in Low Level Measurements of $^{237}\text{Np}/^{239}\text{Np}$ performed in a BGO provided LSC counter

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$^{237}\text{Np}$ in Actinides Separation

Chromatography
Partition

Extraction with Alkylphosphoric acid derivates in organic solvents

Anionic Exchange
$^{237}\text{Np}$ in Actinides Separation

Most used tracers

Pu-236 or Pu-242
Am-243
U-232
Th-299
Np ???

Most common Precipitation with: Oxalate, Phospate

Most common measurement method: Alpha Spectrometry

Important variability in the results (from 76 to 90%) due to chemical separation, electrodeposition step or both
$^{237}\text{Np}$ in Actinides Separation

- **Fe (OH)$_3$ (in ammonium) to pH=10**
- **$^{239}\text{Np}$ Tracer Addition to the sample**
- **Disolution in HNO3 to final 2.5 M**
- **Ascorbic Acid to final 0.1M**
- **Sulfamic Acid to final 0.1M**
- **Chromatography Separation**
$^{237}$Np in Actinides Separation

TEVA

U-TEVA

TRU -spec
$^{237}$Np in Actinides Separation

1) 5ml 0.05M Ascorb. plus 0.05M sulfamic acid
2) 5ml 2.5M HNO3
3) 15ml 0.02M HNO3 0.02M HF

TEVA

Evaporation of the aq lyer and dissolution in 3 ml (weighed) of 2M HNO3

DISCARD

EVAP. TO DRYNESS AND DISSOLUTION IN 8M HNO3 5 ml

TTA – Pa-233 – Extr.
$^{237}\text{Np in Actinides Separation}$

Weight 2 g from the last dissolution in a plastic vial and mix with 15 ml of UG-AB

LSC with Alpha/Beta Discrimination

24 hs Gamma Measurement
$^{239}\text{Np}$ TRACER PREPARATION

$^{239}\text{Np}$ separation from $^{243}\text{Am}$ standard source

On a TEVA resin and weighing the final elution

Calibration of the resulting solution by Gamma Spec.

Storage of the $^{243}\text{Am}$ percolated

Addition of approximately 1 Bq of tracer to samples, by weight
**Discriminator Set Up**

Beta emitter: \(^{239}\text{Np}\) separated as previously described

Alpha emitter: \(^{237}\text{Np}\) separated as previously described just TEVA +TTA steps

**INSTRUMENT SETTINGS** (Perkin-Elmer TR-3180 supplied with BGO shield and a Perkin Elmer 2900/AB)

Normal Count Mode

Delay Before Burst: 75 nSec
# Calibration Set Up

<table>
<thead>
<tr>
<th>TR-3180 DISCRIMINATOR SET: 183 nSec</th>
<th>TR-2900 DISCRIMINATOR SET: 138 nSec</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Alpha Spillover: 37.25%</td>
<td>% Alpha Spillover: 36.86%</td>
</tr>
<tr>
<td>%Beta Spillover: 37.47%</td>
<td>%Beta Spillover: 37.26%</td>
</tr>
</tbody>
</table>
Spectra obtained in the set up of the method

$^{239}$Np in the TR-2900 A/B counter: NCM and DBB = 75 nsec

Beta channel

Alpha channel
Spectra obtained in the set up of the method

$^{239}$Np in the TR-2900 A/B counter: **HSCM** and DBB = 75 nsec

Beta channel

HSCM effect

Slight decrease in counting

Alpha channel
Spectra obtained in the set up of the method

$^{237}$Np in the TR-2900 A/B counter: NCM and DBB = 75 nsec

Reg1 = 0 - 252
Reg2 = 100-252
Reg3 = 100-180
Reg4 = 180-252
Spectra obtained in the set up of the method

$^{237}$Np in the TR-2900 A/B counter: HSCM and DBB = 75 nsec

Reg1 = 0 - 252
Reg2 = 100-252
Reg3 = 180-252
Reg4 = 100-180
Influence of the DBB in the ratio $\beta_\alpha / \beta_T$

$^{239}\text{Np TR-3180 : LLCM}$

(37 Bq in the vial)
**Influence of the DBB (nsec) in the ratio $\beta_\alpha / \beta_T (^{239}N_\rho)$**

<table>
<thead>
<tr>
<th>DBB</th>
<th>t-SIE</th>
<th>$\beta_{5-300}$ cpm</th>
<th>$\alpha_{100-180}$ cpm</th>
<th>$\alpha_{180-252}$ cpm</th>
<th>$\alpha_{100-252} / \beta_{5-300}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>438.1</td>
<td>103.2</td>
<td>136.3</td>
<td>105.7</td>
<td>2.34</td>
</tr>
<tr>
<td>100</td>
<td>429.7</td>
<td>131.4</td>
<td>126.2</td>
<td>113.1</td>
<td>1.82</td>
</tr>
<tr>
<td>200</td>
<td>433.1</td>
<td>193.6</td>
<td>129.1</td>
<td>100.1</td>
<td>1.18</td>
</tr>
<tr>
<td>300</td>
<td>434.6</td>
<td>237.6</td>
<td>128.5</td>
<td>105.8</td>
<td>0.99</td>
</tr>
<tr>
<td>400</td>
<td>430.5</td>
<td>236.5</td>
<td>132.8</td>
<td>112.6</td>
<td>1.03</td>
</tr>
<tr>
<td>500</td>
<td>434.2</td>
<td>286.8</td>
<td>120.8</td>
<td>111.5</td>
<td>0.81</td>
</tr>
<tr>
<td>600</td>
<td>437.0</td>
<td>297.2</td>
<td>131.5</td>
<td>98.2</td>
<td>0.77</td>
</tr>
<tr>
<td>700</td>
<td>433.5</td>
<td>312.7</td>
<td>133.7</td>
<td>107.8</td>
<td>0.77</td>
</tr>
<tr>
<td>800</td>
<td>429.9</td>
<td>319.4</td>
<td>133.2</td>
<td>100.3</td>
<td>0.73</td>
</tr>
<tr>
<td>Average</td>
<td>429.9 +/- 2.8</td>
<td>130.23 +/- 4.7</td>
<td>106.1 +/- 5.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**RATIO**: $\alpha_{100-252} / \text{Gamma spect} = 236.3/2322 = 10.2\%$
Influence of the DBB (nsec) in the ratio $\alpha\beta / \alpha_T (^{237}N_p)$

Total count in the vial (NCM, DBB = 75 nSec, Wdw= 100-252, tSIE= 430.5) 1620 CPM as a reference for 100% in Eff.

<table>
<thead>
<tr>
<th>DBB (nSec)</th>
<th>t-SIE</th>
<th>$\text{CPM}_\beta$ 100-252</th>
<th>$\text{CPM}_\alpha$ 100-252</th>
<th>% Spillover</th>
<th>Eff$\alpha$ 100 -252</th>
<th>Eff ($\alpha+\beta$) 100-252</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>428.6</td>
<td>12.6</td>
<td>733.0</td>
<td>1.7</td>
<td>45.2</td>
<td>46.0</td>
</tr>
<tr>
<td>100</td>
<td>428.9</td>
<td>67</td>
<td>726.7</td>
<td>8.4</td>
<td>44.8</td>
<td>48.8</td>
</tr>
<tr>
<td>200</td>
<td>430.1</td>
<td>125.4</td>
<td>734.7</td>
<td>14.6</td>
<td>45.4</td>
<td>53.1</td>
</tr>
<tr>
<td>300</td>
<td>433.2</td>
<td>192.2</td>
<td>734.2</td>
<td>20.6</td>
<td>45.3</td>
<td>57.2</td>
</tr>
<tr>
<td>400</td>
<td>428.4</td>
<td>319.7</td>
<td>760.9</td>
<td>29.6</td>
<td>46.9</td>
<td>66.7</td>
</tr>
<tr>
<td>500</td>
<td>429.0</td>
<td>509.1</td>
<td>740.7</td>
<td>40.7</td>
<td>45.7</td>
<td>77.1</td>
</tr>
<tr>
<td>600</td>
<td>431.5</td>
<td>637.0</td>
<td>775.0</td>
<td>45.1</td>
<td>47.8</td>
<td>87.2</td>
</tr>
<tr>
<td>700</td>
<td>430.3</td>
<td>783.4</td>
<td>742.1</td>
<td>51.4</td>
<td>45.8</td>
<td>94.2</td>
</tr>
<tr>
<td>800</td>
<td>430.0</td>
<td>865.9</td>
<td>730.1</td>
<td>54.0</td>
<td>45.1</td>
<td>98.5</td>
</tr>
</tbody>
</table>
**Influence of the DBB (nsec) in the ratio LSC vs Gamma at Beta region (5-252 kev) and Blanks (100 min) in beta and alpha region**

<table>
<thead>
<tr>
<th>DBB</th>
<th>BLANK cpmα</th>
<th>BLANK cpmβ</th>
<th>$\frac{\beta_{(5-252)}}{\gamma}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>0.10</td>
<td>1.1</td>
<td>4.4</td>
</tr>
<tr>
<td>100</td>
<td>0.13</td>
<td>1.1</td>
<td>5.6</td>
</tr>
<tr>
<td>200</td>
<td>0.40</td>
<td>5.4</td>
<td>8.4</td>
</tr>
<tr>
<td>300</td>
<td>0.37</td>
<td>6.4</td>
<td>10.2</td>
</tr>
<tr>
<td>400</td>
<td>0.40</td>
<td>5.1</td>
<td>10.9</td>
</tr>
<tr>
<td>500</td>
<td>0.50</td>
<td>7.1</td>
<td>12.4</td>
</tr>
<tr>
<td>600</td>
<td>0.50</td>
<td>7.9</td>
<td>12.8</td>
</tr>
<tr>
<td>700</td>
<td>0.60</td>
<td>8.1</td>
<td>13.5</td>
</tr>
<tr>
<td>800</td>
<td>0.60</td>
<td>8.3</td>
<td>13.8</td>
</tr>
</tbody>
</table>
Influence of quench at a fixed DBB (600 nSec)

Quencher agent: 2.5M HNO₃
Influence of quench at a fixed DBB (600 nSec)
Influence of quench at a fixed DBB (600 nSec)

BETA EFFICIENCY IN THE ALPHA REGION (100-252)

Rank 3 Eqn 47 $y^1 = a + bx^2 \ln x$

Count referred to 2322 dpm

<table>
<thead>
<tr>
<th>Count (100-252)</th>
<th>% Eff.</th>
<th>t-SIE</th>
</tr>
</thead>
<tbody>
<tr>
<td>236.3</td>
<td>10.2</td>
<td>429.9</td>
</tr>
<tr>
<td>195.0</td>
<td>8.4</td>
<td>425.0</td>
</tr>
<tr>
<td>166.8</td>
<td>7.2</td>
<td>421.3</td>
</tr>
<tr>
<td>162.0</td>
<td>6.9</td>
<td>419.8</td>
</tr>
<tr>
<td>140.0</td>
<td>6.0</td>
<td>414.5</td>
</tr>
<tr>
<td>97.0</td>
<td>4.1</td>
<td>393.0</td>
</tr>
</tbody>
</table>
What would be an acceptable tracer amount?

For a maximum recovery of 90%

Gamma measurement of 0.5 Bq (24 hs with an error <10%)

Assuming the best efficiency obtained in the alpha region for $^{239}$Np (10.2%)

$$A = \frac{0.5}{0.9} \times \frac{3}{2} = 0.8 Bq$$
What would be an acceptable tracer amount?

$^{239}\text{Np}$ counting in the region alpha: 2.3 cpm
taking into account 1 day of decay

$$\text{BKG}_{(100-252)} = 2.3 + 0.5 = 2.8 \text{ cpm}$$
What is the Minimum Detectable Activity for $^{237}\text{Np}$?

Assuming that the variance of blank (0.5 cpm) and that of (tracer + blank) and random errors follow a gaussian distribution

Approaching by Currie’s model.

$$MDA = \left(2.71 + 2 \times 1.645 \sqrt{S_B^2 + S_{(T+B)}^2}\right) \times 3 = 0.07 \text{Bq/l}$$

$$t = 100 \text{ min}, \quad R_\gamma = 90\%, \quad V_s = 0.5 \text{l} \quad \text{Eff.} = 45.8\%$$
What is the Minimum Detectable Activity for $^{237}\text{Np}$?

1) Preparation of a 8.0 Bq (+/-1%)/100ml standard solution of $^{239}\text{Np}$

2) Addition of 10ml (by weight) to blank water samples (increasing amount every day)

3) Processed as described.

4) Gamma measurement 24 hs

5) Liquid Scintillation measurement
## Experimental Results

<table>
<thead>
<tr>
<th>$R\gamma$</th>
<th>$t$-SIE</th>
<th>$\gamma_{\text{Eff.}}$ (100-252)</th>
<th>$CPM_{(T+B)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>80.0</td>
<td>425.1</td>
<td>8.35</td>
<td>2.70</td>
</tr>
<tr>
<td>81.0</td>
<td>427.3</td>
<td>9.09</td>
<td>2.89</td>
</tr>
<tr>
<td>83.5</td>
<td>425.5</td>
<td>8.48</td>
<td>2.40</td>
</tr>
<tr>
<td>84.0</td>
<td>428.0</td>
<td>7.34</td>
<td>3.10</td>
</tr>
<tr>
<td>80.1</td>
<td>430.2</td>
<td>10.3</td>
<td>2.64</td>
</tr>
</tbody>
</table>
Experimental Results

\[ Av(cpm) = 2.75 \quad S (cpm) = 0.26 \]

\[ Blank(cpm) = 0.50 \quad S (cpm) = 0.07 \]

\[ \sqrt{(0.26^2 + 0.07^2)} = 0.27 \quad (cpm) \]

\[ MDA = \left( \frac{2.71 + 2 \times 1.645 \sqrt{S_B^2 + S_{(T+B)}^2}}{R_{\gamma} \times E_{\text{eff}} \times t \times 60 \frac{dpm}{Bq} \times 2 \times V_s} \right) \times 3 = 0.12 \text{ Bq/l} \]

SQR converted to counts
## Experimental Results

Spike of water samples at the experimental MDA level

<table>
<thead>
<tr>
<th>$^{237}$Np (Bq)/l</th>
<th>$^{239}$Np (Bq)</th>
<th>$t$-SIE</th>
<th>$\gamma$ Eff $(100-252)$</th>
<th>CPM $(100-252)$</th>
<th>Result Bq/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.153</td>
<td>0.810</td>
<td>420.6</td>
<td>7.18</td>
<td>4.10</td>
<td>0.18 +/- 18.5%</td>
</tr>
<tr>
<td>0.135</td>
<td>0.805</td>
<td>421.7</td>
<td>7.43</td>
<td>3.95</td>
<td>0.16 +/- 18.5%</td>
</tr>
<tr>
<td>0.161</td>
<td>0.812</td>
<td>430.1</td>
<td>10.2</td>
<td>5.74</td>
<td>0.40 +/- 17.5%</td>
</tr>
<tr>
<td>0.125</td>
<td>0.802</td>
<td>420.3</td>
<td>7.11</td>
<td>3.57</td>
<td>0.11 +/- 19.5%</td>
</tr>
<tr>
<td>0.127</td>
<td>0.804</td>
<td>428.7</td>
<td>9.6</td>
<td>3.72</td>
<td>0.13 +/- 19.0%</td>
</tr>
</tbody>
</table>
Experimental Results

The uncertainty percent was calculated taking into account only:

Recovery = 81.7% +/- 2.3%

Alpha efficiency: 45.8 % +/- 2.2%

\[ S_{cpm(t+B)} = 275 \text{ cpm} \quad +/- \quad 9.0\% \]

\[ \sigma_{(cpm)\text{alpha}} = \frac{\sqrt{N}}{N} * 100 \]
CONCLUSION

$^{237}$Np may be traceable by using $^{239}$Np fresh prepared and calibrated but some consideration should be taken into account.

Under a precise control of quench variable as well as a reliable pre-calibrated standard of $^{239}$Np, gamma measurements are an useful tool to determine low amounts of tracer with acceptable precision.

The MDA obtained fits for the purpose though is a little bit higher than for alpha spectroscopy.
CONCLUSION

Although results at the MDA level seem to agree the previous calculation based on experimental data, it is necessary to focus a better fitting in the calibration curve of Eff vs Spillover in the alpha region. However, validation assays must go on in order to have a better statistical support.

An extra effort should be done in order to be able to measure $^{239}$Np in the beta region free of missclassified alpha emission.
THANK YOU VERY MUCH FOR YOUR ATTENTION