# Extension of DOSY to <sup>77</sup>Se NMR

### F. Hallwass\*, R. O. Silva, S. M. C. Gonçalves, P.H. Menezes, A. M. Simas

Departamento de Química Fundamental - UFPE - Recife - Pernambuco, Brazil hallwass@ufpe.br

# Keywords: 77Se NMR; DOSY

**Abstract:** The natural abundance of <sup>77</sup>Se is 7.5%, approximately six times greater than <sup>13</sup>C. Furthermore, the sensitivity of <sup>77</sup>Se nucleus is three times higher than that of <sup>13</sup>C. Thus, <sup>77</sup>Se is an interesting nucleus for NMR studies - DOSY experiments included. Accordingly, we prepared a sample with both non-enriched diphenyldiselenide, and selenophene in CDCl<sub>3</sub>. <sup>77</sup>Se DOSY experiments were performed at room temperature (25°C) at a frequency of 57,24 MHz using a 5 mm PFG (Pulsed Field Gradient) probe equipped with a z-axis gradient amplifier with active shielding coil, in a 7,04 T Varian Unity plus spectrometer. DgcsteSL pulses sequence was used; 64 transients were collected for each of 20 gradient values; and the gradient strength was varied between 1 and 45 Gcm<sup>-1</sup>; 2,1 ms rectangular gradients pulses were used and the diffusion time  $\Delta$  was set at 2,5 s. The recycling delay time was 45 s (5.T<sub>1</sub>) and the total acquisition time was 16,5 hours. To assess the consistency of our measured <sup>77</sup>Se diffusion coefficient, we compared these values with the equivalent <sup>1</sup>H DOSY ones, i.e., with a firmly established technique for the same sample. The results obtained for the diffusion coefficients for both <sup>77</sup>Se and <sup>1</sup>H were the same, within the error bars. It was also found that , <sup>77</sup>Se DOSY can be alternatively used in cases where proton DOSY experiments are poorly resolved.

The result of DOSY<sup>1</sup> (Diffusion Ordered Spectroscopy) is a two-dimensional spectrum where chemical shifts (on the horizontal axis) and diffusion constants (on the vertical axis) for a mixture can be obtained simultaneously, so that the diffusion coefficients of species can determined resembling be а chromatographic separation. Thus, DOSY experiments can, and have indeed been used, molecular interactions<sup>2</sup> study and to associations.3

The natural abundance of <sup>77</sup>Se is 7.5%, approximately six times greater than that of <sup>13</sup>C. Furthermore, the sensitivity of <sup>77</sup>Se nucleus is three times higher than that of <sup>13</sup>C.<sup>4</sup> Thus, <sup>77</sup>Se is an interesting nucleus for NMR studies - DOSY experiments included. Accordingly, we prepared a sample with both non-enriched diphenyldiselenide (0.1092 g), **1**, and selenophene (0.159 g), **2** in CDCl<sub>3</sub>.



<sup>77</sup>Se DOSY experiments were carried out at room temperature (25°C) at a frequency of 57.24 MHz using a 5 mm PFG (Pulsed Field Gradient) probe equipped with a z-axis gradient amplifier with active shielding coil, in a 7.04 T Varian Unity plus spectrometer. <sup>77</sup>Se spectra were referenced at 462 ppm to diphenyldiselenide, in CDCl<sub>3</sub>, as an external standard. DgcsteSL pulses sequence was used; 64 transients were collected for each of 20 gradient values; and the gradient strength was varied between 1 and 45 Gcm<sup>-1</sup>; 2.1 ms rectangular gradients pulses were used and the diffusion time  $\Delta$  was set at 0.25 s. The recycling delay time was 45 s (5xT<sub>1</sub>) and the total acquisition time was 16.5 hours.

T<sub>1</sub> was determined for the studied nucleus, using the inversion recovery pulse sequence:  $(\pi - \tau - \pi/2)$ . The values for <sup>77</sup>Se chemical shift and diffusion coefficient were, respectively, 462.8 ppm and 1.79x10<sup>-9</sup> m<sup>2</sup>s<sup>-1</sup> for the diphenyldiselenide and 611.1 ppm and 2.13x10<sup>-9</sup> m<sup>2</sup>s<sup>-1</sup> for selenophene.



To assess the consistency of our measured <sup>77</sup>Se diffusion coefficient, we compared these values with the equivalent <sup>1</sup>H DOSY ones, *i.e.*, with a firmly established technique, for the same sample. The obtained results for the diffusion coefficients for both <sup>77</sup>Se and <sup>1</sup>H were

the same, within the error bars. It was also found that <sup>77</sup>Se DOSY can be alternatively used in cases where proton DOSY experiments are poorly resolved.

### Acknowledgements

The authors thank UFPE, CNPq, PROFIX and Instituto do Milênio de Materiais Complexos.

### References

- K.F. Morris, C.S. Johnson, J. Am. Chem. Soc. 114 (1992) 3139.
- 2. G.S. Kapur, E.J. Cabrita, S. Berger, *Tetrahedron Lett.* **41** (2000) 7181.
- 3. I. Keresztes, P.G. Williard, *J. Am. Chem. Soc.* **122** (2000) 10228.
- H. Duddeck, Progress in NMR Spectroscopy, 27 (1995) 1.