TEMPERATURE COEFFICIENTS AS A TOOL FOR SPECTRAL ASSIGNMENT

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Assignment of NMR spectra is needed to solve various problems e.g. to identify compounds in metabolomic mixtures or to confirm the structures of new compounds after chemical synthesis. 1D and 2D NMR provide information about chemical shifts and correlations. However, some ambiguities in assignment process may be still present. Thus, having more nuclei-specific spectral parameters would be useful.

In protein studies, researchers often measure temperature coefficients (TCs), i.e. the rates of change of chemical shifts with temperature. They indicate the exposure of amide protons to solvent exchange, presence of low-populated excited states and other phenomena. We show, that TCs can be used in the analysis of small molecules, such as metabolites,[1] and to support the spectral assignment of groups of similar compounds.

Therefore, we propose simple ^{1}H variable-temperature (VT) measurements whose time can be the same or even shorter than the those of the conventional 2D spectra. We present two approaches: 1) TCs for metabolites identification in natural mixture (plasma) based on serum's TCs and 2) TCs from one assigned molecule (Figure 1A) transferred to another, very similar molecule. We show, that TCs are consistent and reproducible between samples. For metabolomics studies (Figure 1B), combining with Radon transform processing[2] provided extra increase in signal-to-noise ratio. We believe that in future, it might be one of the trustworthy stages of analysis.

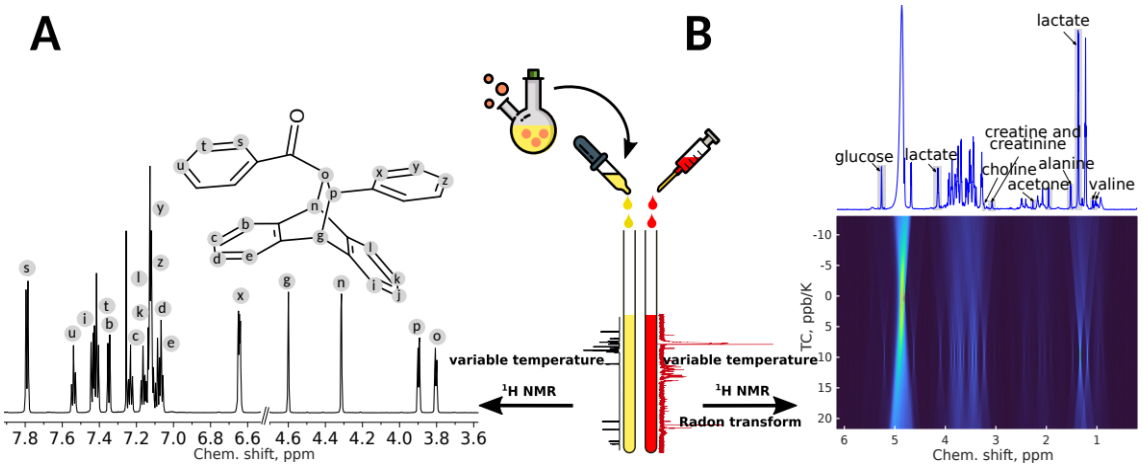

Figure 1. Usefulness of variable temperature ^{1}H NMR in spectral assignment for organic synthesis (A) and metabolomics (B).

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REFERENCES

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[2] Ē. Kupče, R. Freeman, *J. Am. Chem. Soc.* **2013**, *135*(*8*), 2871–2874.