# Advanced Analysis of Isobaric Heat Capacities by Mathematical Gnostics

Z. Wagner, M. Bendová, J. Rotrekl, J. Řezníčková

INSTITUTE OF CHEMICAL PROCESS FUNDAMENTALS OF THE CAS

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# Aim

- Analysis of our experimental heat capacity data on newly synthesized ionic liquids by using a modern non-statistical method
- Comparison of results of repeated series of measured data

# Why to use a non-statistical approach?

- Derived for infinite data sets
- Extrapolated to finite data samples
- Extrapolation to small data samples not adequate
- Prior knowledge of the distribution function of experimental errors required
- Test of normality and Kolmogorov-Smirnov test not applicable to small data samples
- The Central Limit Theorem cannot be used in many cases
- Normal distribution assumed in the most popular statistical methods (arithmetic mean, standard deviation, least squares, t-test, $\chi^2$-test, ANOVA etc.)

# Blind application of an arithmetic mean

$$\frac{\mathrm{CH_3OH} + \mathrm{C_3H_7OH}}{2} = \mathrm{C_2H_5OH}$$

*If you drink methanol + propanol in molar ratio 1 : 1,*
*then in average you drink ethanol.*

# Advantage of mathematical gnostics

- Based on the fundamental laws of nature such as theory of measurement, special theory of relativity, and thermodynamics
- Model of uncertainty derived for each individual measured datum
- Properties of a data sample obtained by aggregation of properties of each single datum, hence valid for small data samples (no extrapolation step needed)
- *Let data speak for themselves!* – No prior assumption of the distribution function of errors, it is estimated during data analysis
- Naturally robust, allows testing data sample homogeneity

# Reliability of gnostic estimates

The reliability (based on data from NIST Webbook Chemistry) was presented in these conferences:

1. Zdeněk Wagner & Pavel Kovanic: *Advanced Data Analysis for Industrial Applications.* Modelling Smart Grids 2015. Prague, September 10–11, 2015,
   *see http://ttsm.icpf.cas.cz/news/conferences.shtml*
2. Pavel Kovanic: *The Mathematical Gnostics – Advanced Data Analysis.* IPMU 2016, Eindhoven, June 20–24, 2016.
   *http://is.ieis.tue.nl/ipmu/*

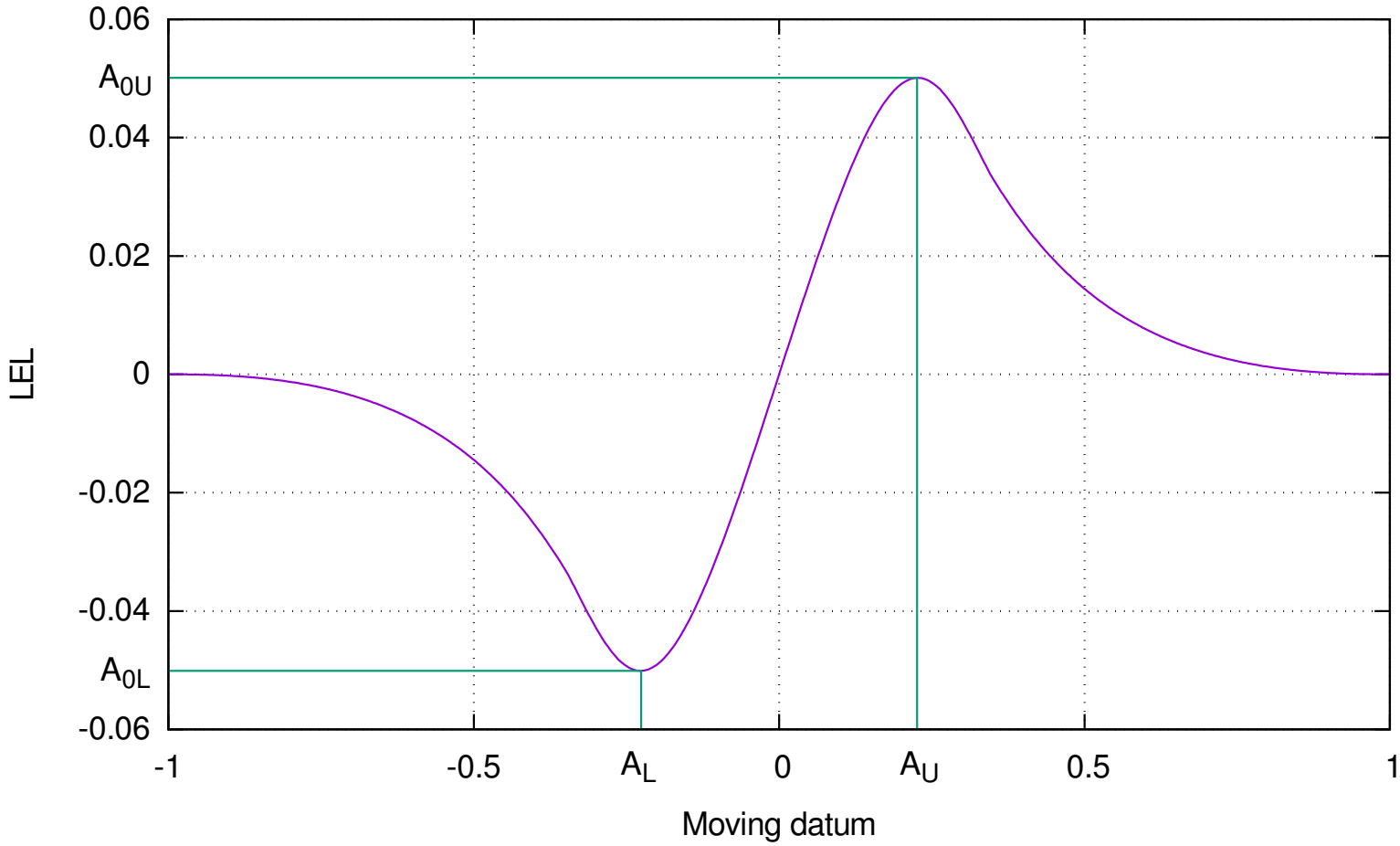
*See also http://www.math-gnostics.com/*
*and follow us on ResearchGate*

# Our first application to heat capacity data

Wagner Z., Andresová A., Bendová M., Machanová K., Rotrekl J.: *Mathematical Gnostics, a Powerful Method of Evaluating Experimental Heat Capacity Data.* 10th International Conference on Distillation and Absorption 2014, Book of Full Papers, pp. 28–33, Friedrichshafen, Germany, 14–17 September 2014.

The work describes mainly the initial setup of the instrument and testing the measurement methods.

# Principles of gnostic marginal analysis




LEL – local estimate of location (maximum probability density)

$(A_L, A_U)$ – interval of typical data

$(A_{0L}, A_{0U})$ – tolerance interval

# Materials

$C_p$ measured for two newly synthesized ionic liquids:

- 1-butyl-3-methoxyethylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4(C_1OC_2)Im][Tf_2N]$)
- 1-butyl-3-(2-(2-ethoxyethoxy)ethyl)imidazolium bis(trifluoromethylsulfonyl)imide ($[C_4(C_2OC_2OC_2)Im][Tf_2N]$)

Purity of both compounds estimated as 97 %.

# Procedure

- $C_p$ measured by using the μDSC 3 Evo microcalorimeter manufactured by Setaram
- Continuous method with heating rate 0.3 K/min
- Measured in steps of 1 K at integer values in degrees Celsius, i. e. at 293.15 K, 294.15 K etc.
- Each series measured four times without refilling the cell (four values of $C_p$ at each value of temperature are available)

# Four series for each IL

**$[C_4(C_1OC_2)Im][Tf_2N]$** :

**d218** sample amount 0.49352 g, temperature range 298.15–378.15 K

**d326** sample amount 1.02973 g, temperature range 298.15–378.15 K

**d401** sample amount 1.15465 g, temperature range 298.15–378.15 K, recycled after evaporation of dichloromethane

**d404** sample amount 1.04197 g, temperature range 298.15-378.15 K, decolorized

**$[C_4(C_2OC_2OC_2)Im][Tf_2N]$** :

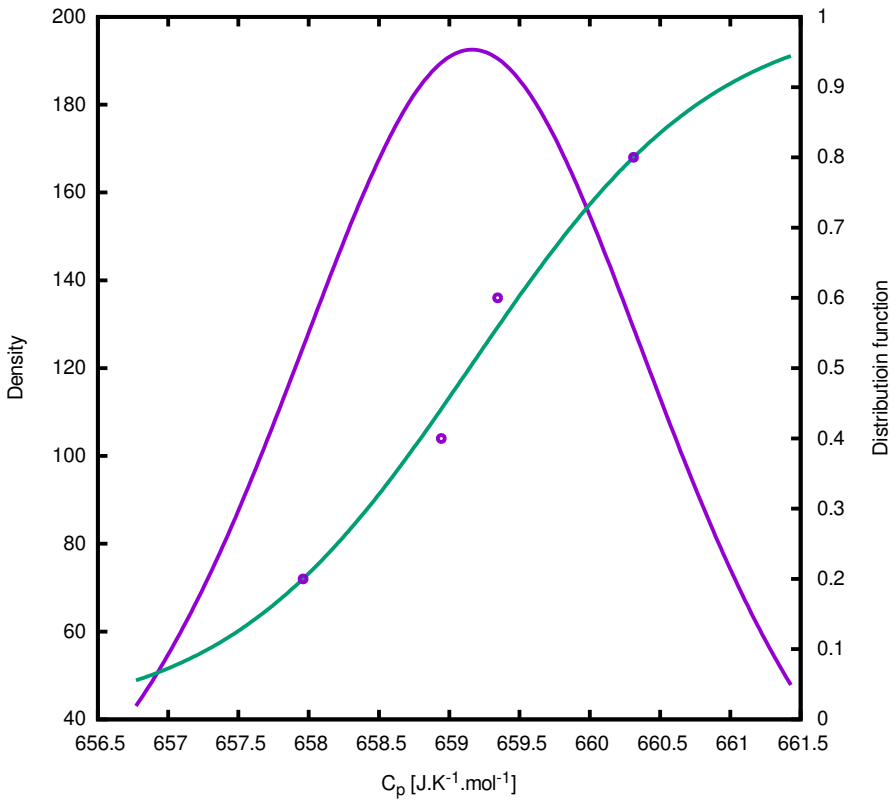
**d127** sample amount 1.01207 g, temperature range 298.15–358.15 K

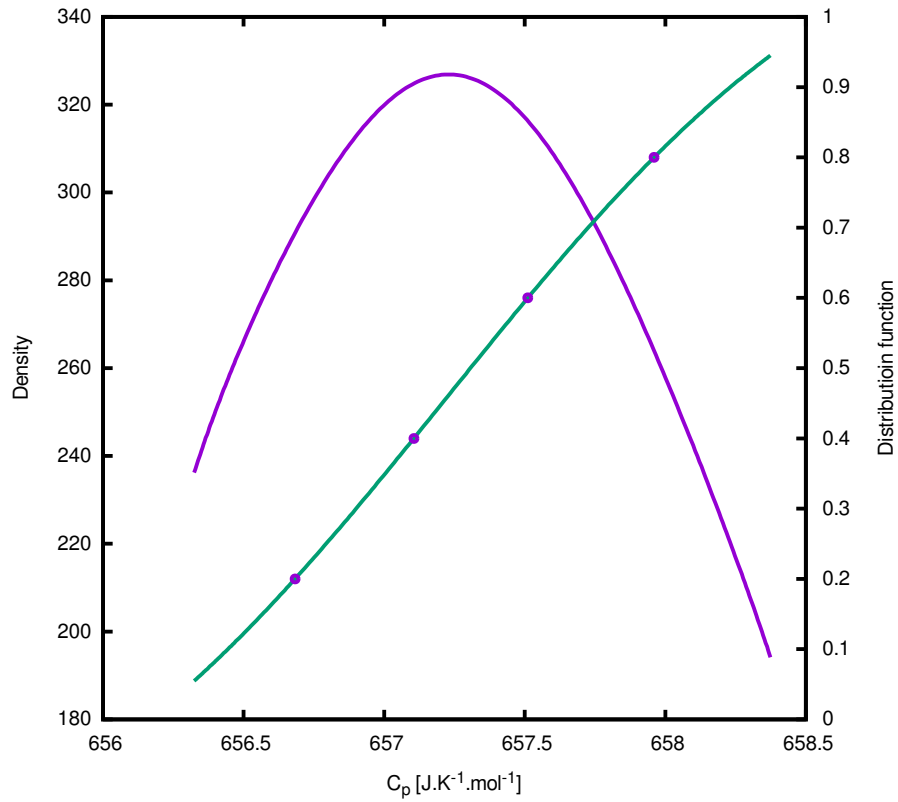
**d129** sample amount 1.02036 g, temperature range 298.15–358.15 K

**d219** sample amount 0.44533 g, temperature range 298.15–378.15 K

**d403** sample amount 1.09433 g, temperature range 298.15–378.15 K, decolorized

# Examples of distribution functions



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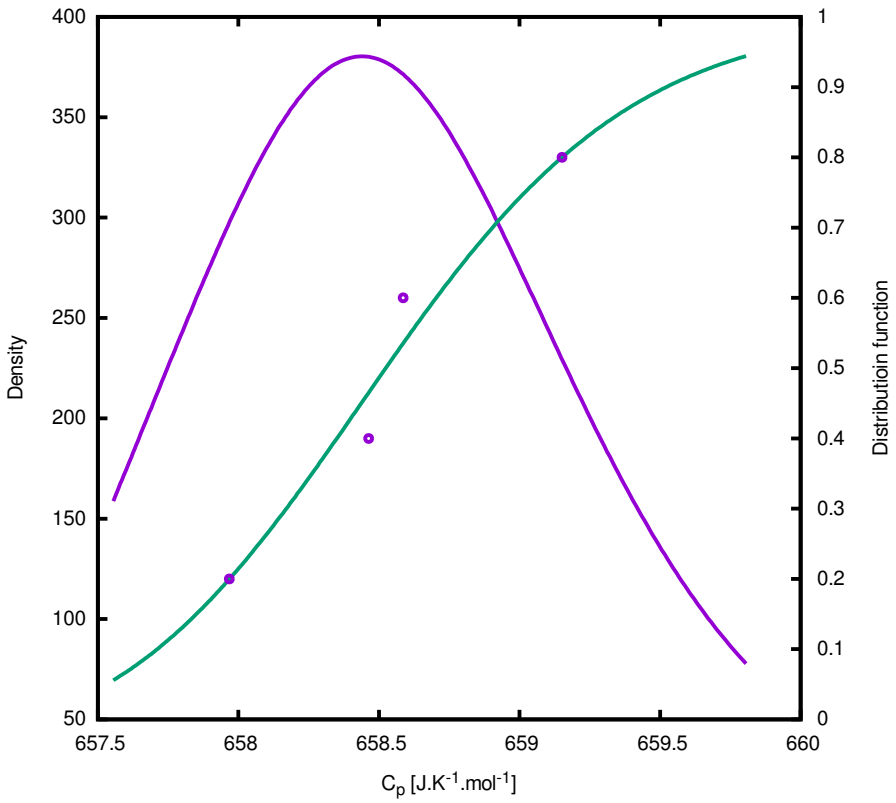


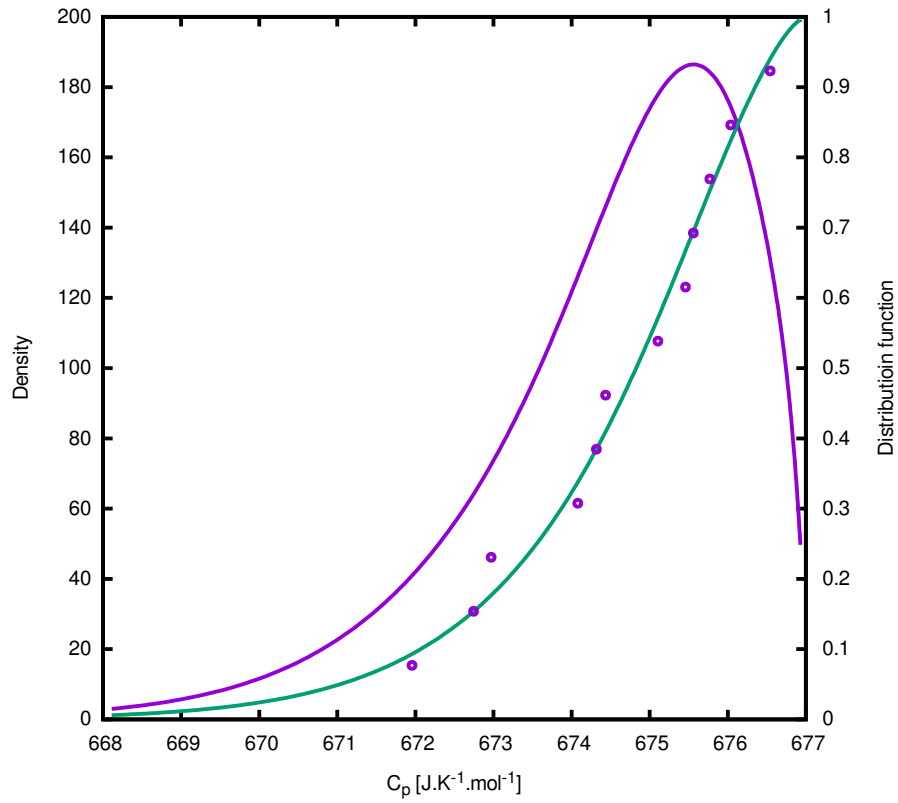

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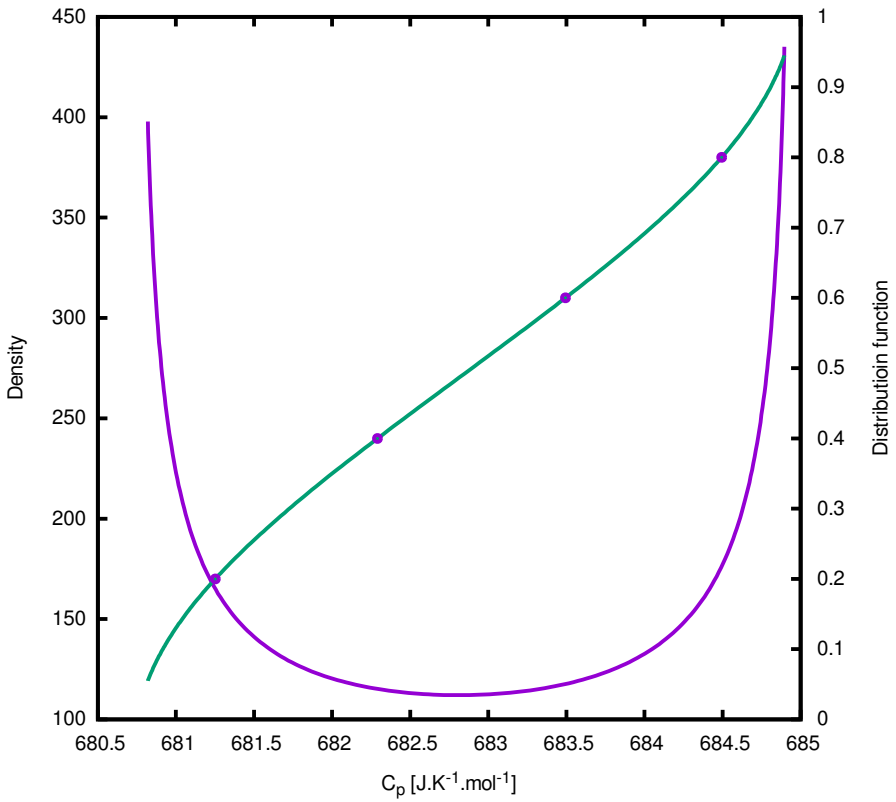
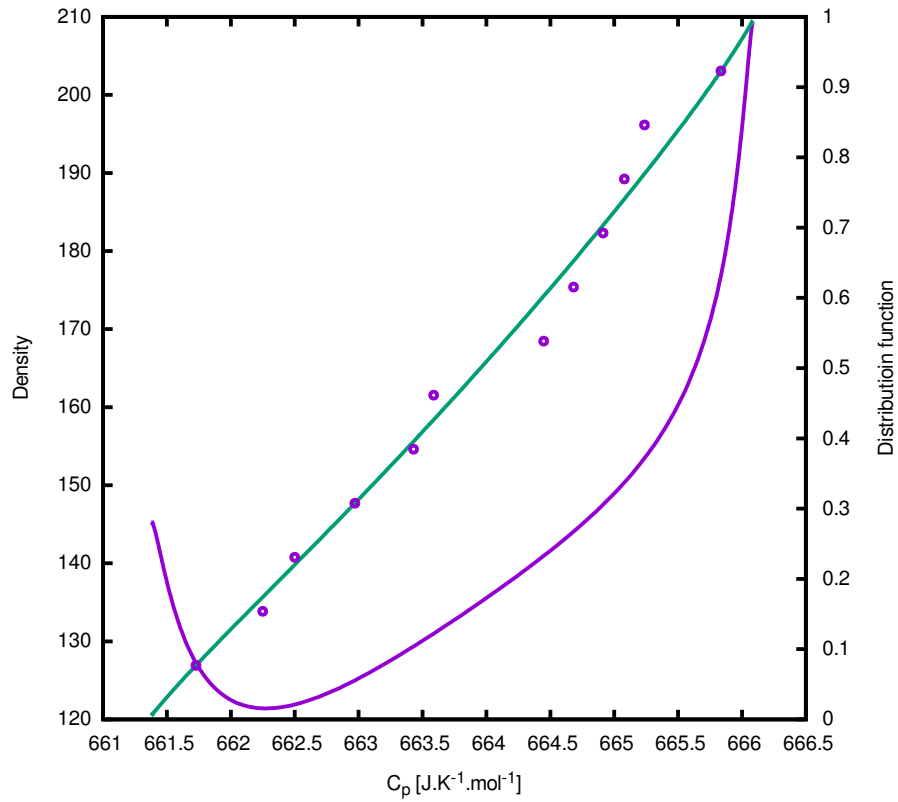
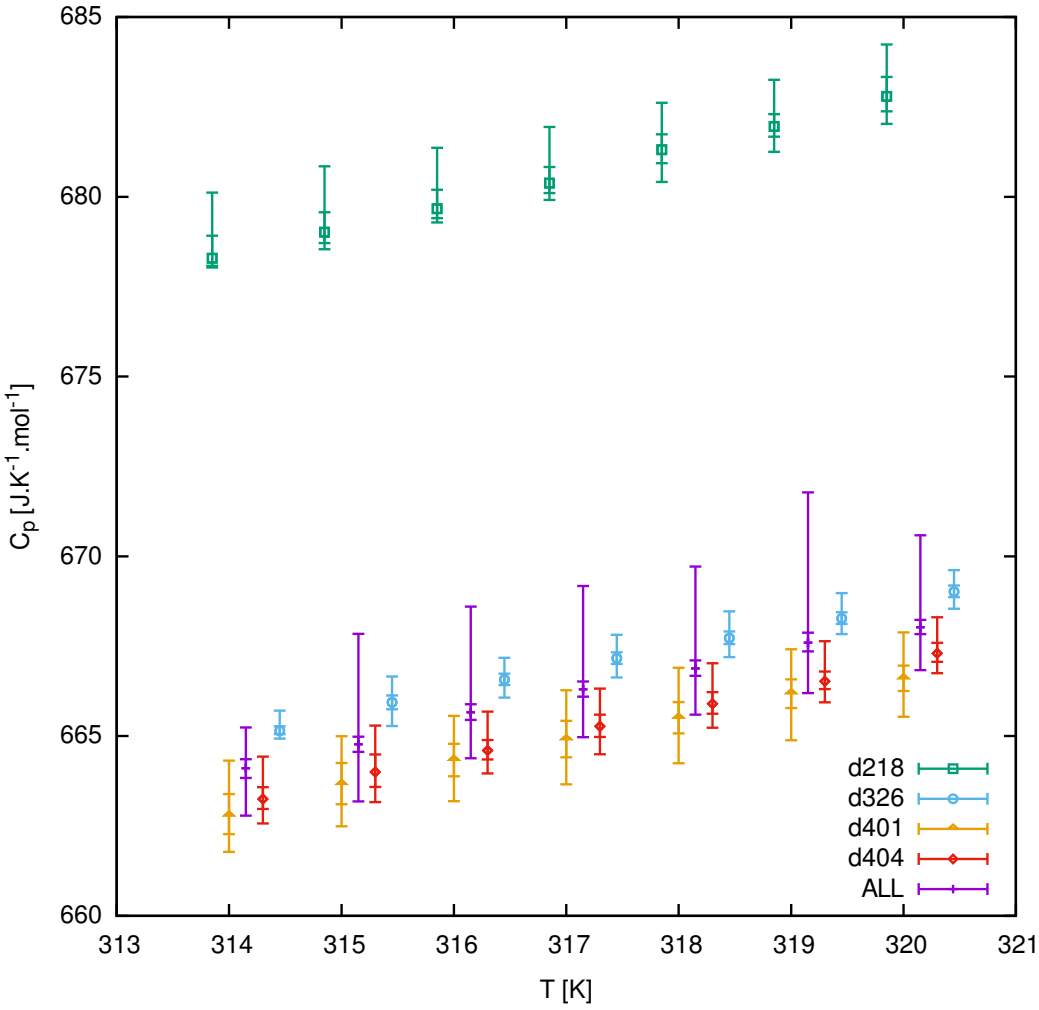


# Comparison of $C_p$ for $[C_4(C_1OC_2)Im][Tf_2N]$




**d218** 0.49352 g

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**ALL** homogeneous subsample of all data

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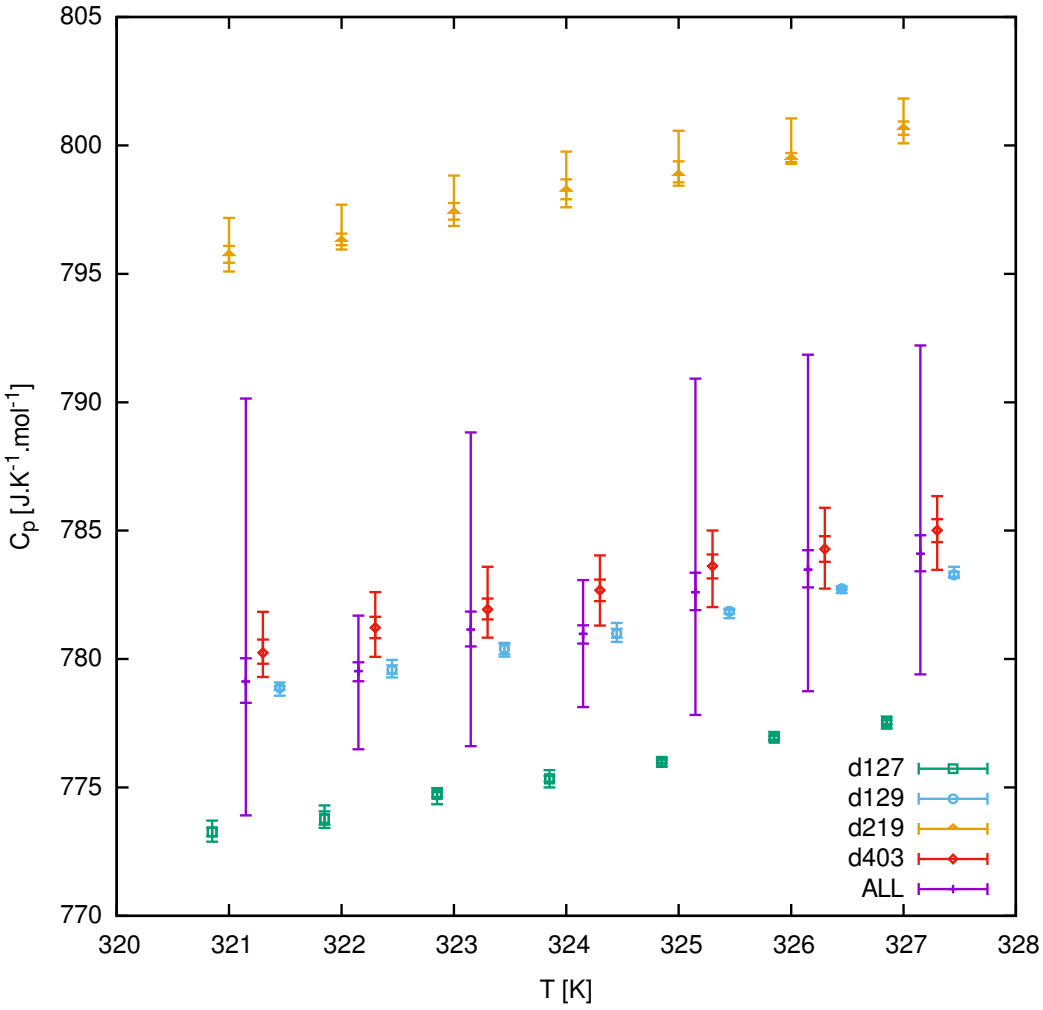


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# Conclusion

- Gnostic marginal analysis proved to provide useful information.
- Keeping the same sample amount is important for obtaining correct results.
- Motivation to future work: identification and quantification of impurities needed.

# Acknowledgement

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*Research Group of Thermodynamics of Task Specific Materials*
*http://ttsm.icpf.cas.cz/*