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# Quantitative mapping of chemical compositions with MRI using compressed sensing

Erik von Harbou [a], Hilary T. Fabich [b], Martin Benning [b,1], Alexander B. Tayler [b], Andrew J. Sederman [b], Lynn F. Gladden [b], Daniel J. Holland [b,*]

[a] Laboratory of Engineering Thermodynamics, University of Kaiserslautern, Erwin-Schrödinger-Straße 44, 67663 Kaiserslautern, Germany
[b] Department of Chemical Engineering and Biotechnology, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, United Kingdom

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ABSTRACT

In this work, a magnetic resonance (MR) imaging method for accelerating the acquisition time of two dimensional concentration maps of different chemical species in mixtures by the use of compressed sensing (CS) is presented. Whilst 2D-concentration maps with a high spatial resolution are prohibitively time-consuming to acquire using full **k**-space sampling techniques, CS enables the reconstruction of quantitative concentration maps from sub-sampled **k**-space data. First, the method was tested by reconstructing simulated data. Then, the CS algorithm was used to reconstruct concentration maps of binary mixtures of 1,4-dioxane and cyclooctane in different samples with a field-of-view of 22 mm and a spatial resolution of 344 μm × 344 μm. Spiral based trajectories were used as sampling schemes. For the data acquisition, eight scans with slightly different trajectories were applied resulting in a total acquisition time of about 8 min. In contrast, a conventional chemical shift imaging experiment at the same resolution would require about 17 h. To get quantitative results, a careful weighting of the regularisation parameter (via the L-curve approach) or contrast-enhancing Bregman iterations are applied for the reconstruction of the concentration maps. Both approaches yield relative errors of the concentration map of less than 2 mol-% without any calibration prior to the measurement. The accuracy of the reconstructed concentration maps deteriorates when the reconstruction model is biased by systematic errors such as large inhomogeneities in the static magnetic field. The presented method is a powerful tool for the fast acquisition of concentration maps that can provide valuable information for the investigation of many phenomena in chemical engineering applications.


## 1. Introduction

Maps of chemical compositions can provide valuable information for many applications, especially in chemical engineering. They can be used to gain a rigorous understanding of chemical processes and mass transfer phenomena occurring, for example, in catalyst beds, along interfaces, or in and near membranes. This understanding is important for a reliable design and scale-up of chemical processes. Taking samples and analysing them *ex situ* is often not feasible because the sampling disturbs the system and the effort is immense to obtain sufficient spatial resolution to resolve the processes. In this application, magnetic resonance imaging (MRI) offers great potential as it is a non-invasive, spatially resolved measurement technique able to probe optically opaque environments like reactors. In situ MRI has been successfully applied to study conversion and composition profiles or local reaction rates along fixed-bed reactors for various reactions using spatially resolved $^{1}$H NMR-spectroscopy [1,2] and $^{13}$C NMR-spectroscopy [3–5] also called chemical shift imaging (CSI). The acquisition time needed to obtain multidimensional, fully sampled concentration maps, however, may take several hours [3] which can be detrimental. First, the process has to be operated steadily for several hours so the consumption of chemicals is high which is costly and undesirable concerning the safety in laboratories. Second, transient phenomena that take place within minutes cannot be studied with this technique. This paper presents a method for accelerating the acquisition of spatially resolved concentration maps by the use of compressed sensing (CS).

CS enables the accurate reconstruction of an under-sampled signal by utilising the prior knowledge that the signal is compressible

* Corresponding author at: Department of Chemical and Process Engineering, University of Canterbury, Private Bag, 4800 Christchurch, New Zealand.
*E-mail address:* daniel.holland@canterbury.ac.nz (D.J. Holland).
[1] Current address: Department of Applied Mathematics and Theoretical Physics, University of Cambridge, Wilberforce Road, CB3 0WA Cambridge, United Kingdom.

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or sparse with respect to a specific representation [6,7]. As undersampled signals can be used, CS provides a method of reducing the data acquisition times characteristic of many imaging techniques. CS has been successfully applied to reduce the acquisition time of MR images [8,9]. Holland et al. [10] and Tayler et al. [11] demonstrated the potential of CS by reconstructing velocity images in fixed-bed reactors and of multiphase flow, respectively from fast and under-sampled phase-encoded MR measurements. Furthermore, Holland et al. [12] and Kazimierczuk and Orekhov [13] applied CS for fast multidimensional NMR spectroscopy. Hu et al. [14] and Kampf et al. [15] used CS for the accurate reconstruction of three dimensional chemical shift imaging (CSI) of $^{13}C$ and $^{19}F$ markers, respectively from under-sampled data sets. When the chemical shift information of the observed chemical species is known and is incorporated into the model used for the reconstruction, images showing different species can be directly recovered with high resolution from the under-sampled signals by CS. Good results with a significant reduction of the scanning time compared to conventional methods have been achieved in medical applications with this method for imaging water and fat [16–18]. The focus of these works was to get a good separation of water and fat in the reconstructed images and not to obtain quantitative information on the composition.

In this work, we apply CS reconstruction to resolve spatially and quantitatively the compositions of different species in mixtures. This method enables the mapping of the composition directly as a function of space. Only the information about the chemical shift of the observed species are required for the reconstruction; there is no need for calibration prior to the analysis. This feature of the presented method is beneficial for many applications in chemical engineering where unstable intermediates are formed during the process that make a calibration impossible. To achieve a high accuracy of the concentration map, however, the parameters of the CS algorithm have to be correctly set. As mentioned above, CS exploits prior knowledge of the signal. This prior knowledge is integrated in the CS solver with a regulariser [6,7]. To get quantitative results, the systematic bias of the CS reconstruction has to be minimised, either by carefully weighting the regulariser or by applying contrast-enhancement approaches. Different generic approaches exist for the identification of good regularisation parameters. In the present work, two different approaches, the L-curve approach [19] and the Bregman iterations [20], are applied for the reconstruction of simulated data of a phantom sample and for the reconstruction of measured data from binary mixtures in different test samples. These results are used to assess the robustness of the approaches to yield concentration maps with a high accuracy. Finally, we present a discussion of the strengths and limitations of the method for the spatial quantification of chemical species.

## 2. Reconstruction using compressed sensing

### 2.1. Model equations

The measured **k**-space signal **S** at the echo time $t$ is related to the concentration maps $\mathbf{x}_k$ of all species $k = 1, \ldots, M$ via the signal model [16]

$$\mathbf{S}(t) = \sum_{k=1}^{M}\left(\sum_{j=1}^{L_k} w_{k,j}\exp\left(2\pi i\,\delta_{k,j}t\right)\exp\left(-\frac{t+2\tau}{T_2^*}\right)\times\int_{\Omega}\mathbf{x}_k(\mathbf{r})\exp\left(2\pi i\,\mathbf{k}(\mathbf{t})\cdot\mathbf{r}\right)\mathrm{d}\mathbf{r}\right)+\mathbf{v} \quad (1)$$

with

$$\mathbf{k}(t) = \frac{1}{2\pi}\int_0^t \gamma\mathbf{G}(t')\mathrm{d}t' \quad \text{and} \quad \Omega \subset \mathbb{R}^2. \quad (2)$$

In Eq. (1), **v** is the noise. $\delta_{k,j}$ denotes the relative chemical shift (related to the resonance frequency of the spectrometer) of the $j$-th group (peak) that belongs to species $k$. $w_{k,j}$ is the group weighting factor that exists for all groups $j = 1, \ldots, L_k$ of species $k$. It describes the mole of the nuclei (here $^1H$: $n^{^1H}$) in the $j$-th group per mole of species $k$ ($n_k^{\text{species}}$), see Eq. (3). To get quantitative results from the measured **k**-space signal, the group weighting factors have to be set correctly.

$$w_{k,j} = \frac{n^{^1H}}{n_{k,j}^{\text{group}}}\frac{n_{k,j}^{\text{group}}}{n_k^{\text{species}}}. \quad (3)$$

In Eq. (2), $2\tau$ denotes the time from the excitation pulse to the centre of the echo and $T_2^*$ denotes the apparent $T_2$-relaxation time. **G** is the vector of the magnetic field gradient that acts at the echo time $t$. Here, we subsample the **k**-space $S_{p,q}$ as $S(t)$. Eq. (1) can be abbreviated with linear operators, see Eq. (4). The explicit equations for the operators are given in Appendix A.

$$\mathbf{S} = \mathbf{CHS}\cdot\mathcal{F}_u\cdot\mathbf{x}+\mathbf{v}. \quad (4)$$

In Eq. (4), **CHS** denotes the chemical shift operator, $\mathcal{F}_u$ is the undersampled Fourier transform, and **x** is the concatenated matrix of all concentration maps $\mathbf{x}_k$ with $k = 1 \ldots M$. Eq. (4) can only be applied when spatial and temporal inhomogeneities in the $\mathbf{B}_0$-field are negligible.

### 2.2. Solving strategy

The goal of the reconstruction is to find well resolved concentration maps **x** from the under-sampled **k**-space measurements **S** so that the signal model according to Eq. (4) is fulfilled. In CS, the reconstruction is obtained by solving a Tikhonov-type optimisation problem of the form (for details, see e.g. Benning et al. [21]):

$$\mathbf{x}_{\text{reconstructed}} = \arg\min_{\mathbf{x}}\left\{\frac{1}{2}\|\mathbf{S}-\mathbf{CHS}\cdot\mathcal{F}_u\cdot\mathbf{x}\|_2^2+\sum_{k=1}^{M}\alpha_k J(\Psi\mathbf{x}_k)\right\}. \quad (5)$$

The first term in Eq. (5) is the fidelity term that models Eq. (1). Here $\|v\|_2 := \sqrt{\sum|v(i)|^2}$is the standard Euclidean 2-norm. The second term is the regularisation with $J(\Psi\mathbf{x}_k)$ as regularisation functional that enables the incorporation of prior information on the reconstruction. $\Psi$ is a linear operator that transforms the concentration maps **x** to another domain where they are sparse. Thus, the solution of Eq. (5) yields concentration maps that have a sparse representation in the transform domain and that are, according to Eq. (1), consistent with the measured **k**-space data in the least squares sense. The parameter $\alpha_k$ is a positive regularisation parameter that weights the influence of the fidelity and the regularisation term. We found that quantitative reconstruction results are only obtained when the parameters $\alpha_1, \alpha_2, \ldots, \alpha_M$ are not chosen independently but based on the group weighting factors $w_{k,j}$ and a constant positive regularisation parameter $\alpha$,

$$\alpha_k = \alpha\sum_{j=1}^{L_k} w_{k,j}. \quad (6)$$

The concentration maps of the test samples used in the present work to test the method contain sharp edges. Thus, a finite-difference approximation of the gradient operator is used as the sparsifying transform $\Psi$ for all reconstructions carried out in this work. For a discrete, isotropic total variation the regularisation functional becomes $J(\Psi x_k) = \|\Psi x_k\|_{2,1} = \|\|\Psi x_k\|_2\|_1$. (details of the computation of this term are given in Appendix B) Depending on the features of the concentration maps, further sparsifying transforms, such as wavelet transforms, which are used for smooth changes in the concentration maps, or other one-norm-based