Magnetic Levitation in Analysis of Foods and Water

SUPPORTING INFORMATION

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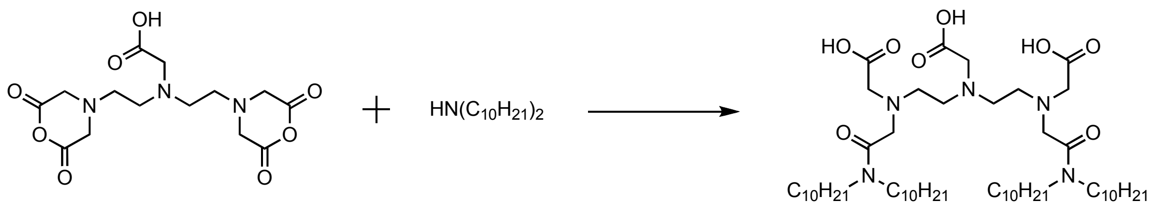
General Methods. The NdFeB magnets (grade N50, 5 cm × 5 cm × 2.5 cm, Model # NB063-N50) were purchased from Applied Magnets (www.magnet4less.com) and positioned 45 mm apart within an aluminum casing. The aluminum casing for the magnets was designed and fabricated by Gaudreau Engineering (West Warwick, RI) for a fee. All chemicals and reagents were purchased from Sigma-Aldrich (Atlanta, GA) and used without further purification, unless noted otherwise. We purchased grains from Whole Foods Market, oils and peanut butter from Whole Foods Market (Cambridge, MA) and Shaw's Supermarket (Cambridge, MA), milk from CVS/pharmacy (Cambridge, MA), and cheese from Trader Joe's (Cambridge, MA). The sample of expressed human milk was voluntarily donated by a lactating female.

Synthesis of Gd(DTAD)

Synthesis of DTAD.



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We added 1.5 mmol of diethylenetriaminepentaacetic acid dianhydride and 3 mmol of didecylamine to 15 mL of anhydrous pyridine (10 mL/mmol), and stirred the solution for 5 minutes until all of the reactants had solubilized. The solution was heated to reflux (~ 117 °C) and stirred under nitrogen for 4 hours. After cooling to room temperature, the majority of the solvent was removed by rotary evaporation. An equal volume of toluene was then added, and the remainder of the solvent was removed. The product was then allowed to dry completely under high vacuum for 16 hours. The final product **1** was obtained as a light brown powder in 98% yield.

^{1}H NMR ($CDCl_3$, 400 MHz): 3.810 (br s, 4H); 3.746 (br s, 6H); 3.244 – 3.210 (br m, 12H); 3.116 (t, J = 7.6 Hz, 4H); 1.486 (m, J = 7.0 Hz, 8H); 1.326 – 1.204 (br m, 56H); 0.877 (t, J = 6.8 Hz, 12H).

^{13}C NMR ($CDCl_3$, 100 MHz, 295 K): δ 13.79, 22.36, 26.59, 26.85, (27.44, 28.56)‡, 29.03, (29.07, 29.13)†, 29.28, 29.36, 31.59, 46.04, 46.96, 50.51, 51.33, 55.31, 168.48, 170.27, 172.90.

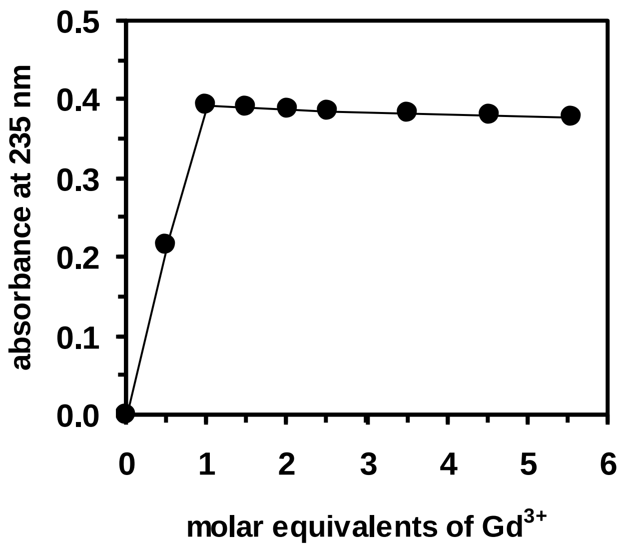
‡/†: These pairs of peaks coalesced at 265.5 K.

HRMS: Found 952.8094 Da and calculated for $C_{54}H_{105}O_8N_5(M+H)^+$ as 952.8036 Da.

Synthesis of Gd(DTAD) Chelate. To 1 mmol of DTAD dissolved in 10 mL of ethanol (10 mL/mmol), 1.05 mmol of $GdCl_3$ dissolved in water (2 mL/mmol) was added dropwise. The solution was stirred at room temperature under a blanket of nitrogen for 4 hours. Equal volumes of water and dichloromethane (DCM) were then added, and the organic layer was extracted twice with DCM. The combined organic fractions were then washed three times with water and dried with $MgSO_4$. The solvent was then removed by rotary evaporation and dried under high vacuum for 16 hours. The final product was obtained quantitatively as an off-white powder. MS: The calculated molecular mass of **Gd(DTAD)** ($C_{54}H_{104}O_9N_5Gd$) was 1124.7092 Da and the measured molecular masses, observed by MALDI, were 562.2067 Da [M+2]/2 and 374.5337 Da [M+3]/3.

Determination of Chelation Stoichiometry. The Gd(DTAD) chelation stoichiometry was determined using UV-Vis spectroscopy by measuring the change in absorbance of a solution of (DTAD) as a function of the introduction of many molar equivalents of Gd^{3+} into the chelating ligand.[1] A solution of 250 mM $GdCl_3$ was titrated (five 5 μL injections and two 10 μL injections) into a 1 mM solution of DTAD in ethanol. Following each injection, the mixture was gently mixed by pipette and allowed to equilibrate for 15 minutes. The UV-Vis absorbance spectrum was monitored from 200 nm to 600 nm for changes indicative of the formation of the Gd-chelate. The greatest absorbance change occurred at 235 nm, and a plot of the absolute change in absorbance, over all injections and corrected for dilution, is shown in **Figure S1**. It is evident that the change in absorbance reaches a maximum at 1 molar equivalent of Gd^{3+} and plateaus at higher equivalents; therefore, the chelation stoichiometry was determined to be 1:1.

Figure S1. A plot of the change in absorbance of a solution of DTAD, monitored at 235 nm, upon the titration of increasing molar equivalents of $GdCl_3$.



Solubility of Gd(DTAD) in Organic Solvents. We determined the solubility by placing solid Gd(DTAD) into a vial and adding solvent in increments until the solids fully dissolved. Gd(DTAD) is soluble (0.5 – 1 M) in many organic solvents including alcohols (ethanol, methanol, octanol), aromatic hydrocarbons (chlorobenzene, nitrobenzene, toluene, 3-fluorotoluene, and related derivatives), polar aprotic solvents (DMF, DMSO, acetonitrile, tetrahydrofuran, diethylether), aliphatic hydrocarbons (hexanes), and their halogenated derivatives (dichloromethane, chloroform, iodomethane, diiodomethane).

Figure S2. Bar graph depicting the chemical composition (per 15 mL) of different kinds of vegetable oils (as obtained from labels provided by the distributor).

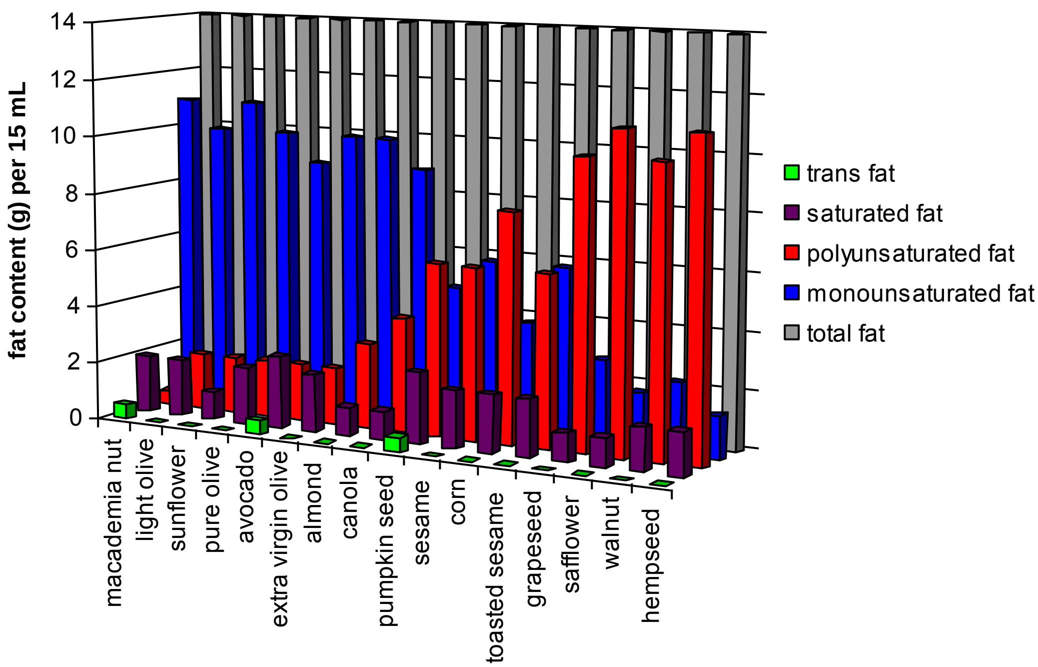
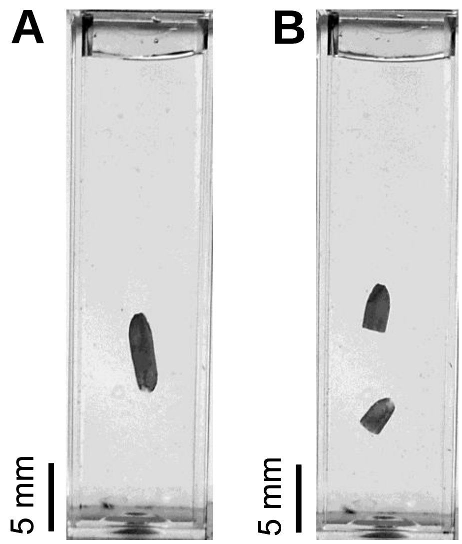


Figure S3. A) Photograph of a grain of brown rice levitating in aqueous 3 M $MnCl_2$. The orientation of the grain is determined by the density distribution within the grain. B) Cutting the rice grain in half results in two different halves that have different densities and levitate at different heights.



Calculating Densities of Samples from Their Levitation Heights. Densities of cheese and peanut butter and the uncertainties in these values were calculated using previously established equations (Equation S1 and S2) and procedures.[2, 3] In these equations, h (m) is the equilibrium levitation height of the sample, ρ_s (kg/m^3) and ρ_m (kg/m^3) are the densities of the sample and of the paramagnetic medium, respectively, g is the acceleration due to gravity, μ_0 (T·m·A^{-1}) is the permeability of free space, d (m) is the distance between the magnets, B_0 (Tesla) is the magnitude of the magnetic field at the surface of the magnets, and χ_m and χ_s (unitless) are the magnetic susceptibilities of the paramagnetic medium and the sample, respectively, T is the ambient temperature, and c is the concentration of the paramagnetic ions in solution. The values of ρ_m and χ_m were computed automatically from c and T using established equations.[2, 4] **Table S0** tabulates the values of these parameters and their uncertainties used for calculating the densities of cheese and peanut butter.

Densities of grains were calculated using a calibration curve: $\rho_s = -0.0039h + 1.4822$; the calibration curve was generated using density standards purchased from American Density Materials, Inc. The uncertainty in density of grains was calculated using Equation S3.[3]

$$\rho_s = \alpha h + \beta \tag{S1}$$

$$\alpha = \frac{4(\chi_s - \chi_m)B_0^2}{g\mu_o d^2} \tag{S1a}$$

$$\beta = \rho_m - \frac{2(\chi_s - \chi_m)B_0^2}{g\mu_o d} \tag{S1b}$$

$$\delta\rho_s = \sqrt{\left(\frac{\partial\rho_s}{\partial T}\delta T\right)^2 + \left(\frac{\partial\rho_s}{\partial c}\delta c\right)^2 + \left(\frac{\partial\rho_s}{\partial \chi_s}\delta\chi_s\right)^2 + \left(\frac{\partial\rho_s}{\partial h}\delta h\right)^2 + \left(\frac{\partial\rho_s}{\partial d}\delta d\right)^2 + \left(\frac{\partial\rho_s}{\partial B_0}\delta B_0\right)^2} \tag{S2}$$

$$\delta\rho_s = \left|\frac{d\rho_s}{dh}\right|\delta h = |\alpha|\delta h \tag{S3}$$

Table S1. Values for experimental parameters used in this study. Values of B_0, d, T, χ_s, g, μ_0 are identical for all the experiments. Values of *c* and *h* typically vary for each analyte. As an example, we use the values of *c* and *h* for levitating "string cheese".

Parameter *P*	Description	Magnitude of *P*	δP
experimental parameters			
B_0	strength of magnetic field at the surface of the magnet	0.375 T	± 0.003 T
d	distance between magnets	45 mm	± 0.5 mm
T	Temperature	23 °C	± 1 °C
c	Concentration of $MnCl_2$	1.000 M	± 0.002 M
Unknowns			
χ_s	bulk magnetic susceptibility of the sample	-5×10^{-6} (SI, unitless)	10×10^{-6} (SI, unitless)
calculated parameters			
$\rho_m(c,T)$	density of paramagnetic medium	1.0994 g/cm^3	± 0.0003 g/cm^3
$\chi_m(c,T)$	bulk magnetic susceptibility of the medium	$\pm 177 \times 10^{-6}$	7.29×10^{-10}
constants			
g	acceleration due to gravity	9.80 m/s^2	n/a
μ_0	permeability of free space	$4\pi \times 10^{-6}$ $N \cdot A^{-2}$	n/a
independent variable			
h	"levitation height" of the sample above the bottom magnet	22.6 mm	± 0.5 mm
dependent variable			
ρ_s	density of sample	1.099 g/cm^3	± 0.002 g/cm^3

Table S2. Tabulated values (average obtained from at least seven independent measurements) of levitation heights and densities of grains levitated in 0.475 M $GdCl_3$ + 4.5 M $CaCl_2$, string cheese levitated in 1.000 M $MnCl_2$, and peanut butter levitated in 1.000 M $MnCl_2$.

sample	h (mm)	ρ_s (g/cm^3)
grains		
white rice	7.1 ± 1.1	1.455 ± 0.004
brown rice	19.0 ± 2.8	1.408 ± 0.004
purple sticky rice	26.1 ± 1.8	1.380 ± 0.004
whole grain kamut	32.8 ± 1.6	1.354 ± 0.004
forbidden rice	15.7 ± 0.4	1.421 ± 0.004
barley (pearled)	28.6 ± 3.7	1.371 ± 0.004
millet (hulled)	31.5 ± 3.9	1.359 ± 0.004
amaranth	29.1 ± 1.7	1.369 ± 0.004
cheese		
string cheese	22.6 ± 0.5	1.099 ± 0.002
low-fat string cheese	14.7 ± 0.6	1.131 ± 0.003
peanut butter		
Skippy's creamy	18.3 ± 1.8	1.117 ± 0.007
Skippy's creamy (reduced fat)	2.1 ± 0.6	1.183 ± 0.005

Figure S4. Plot of fat content versus levitation height for different kinds of bovine milk. The vertical error bars represent maximum deviation from the mean based on three measurements.

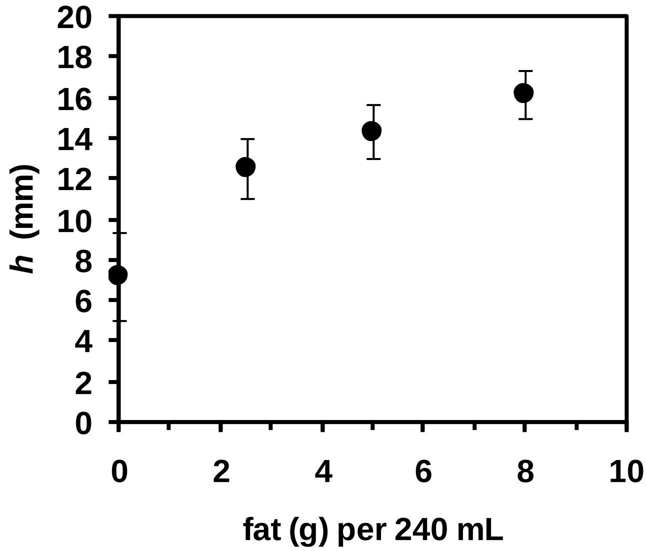


Table S3. Nutritional content and sources of milk used in this study.

label	whole milk	2%	1%	0%
brand	Garelick Farms	Garelick Farms	Garelick Farms	Garelick Farms
serving size	240 mL	240 mL	240 mL	240 mL
calories	150	130	110	90
calories from fat	70	45	20	0
total fat (g)	8	5	2.5	0
saturated fat (g)	5	3	1.5	0
cholesterol (mg)	35	20	10	5
sodium (mg)	120	130	130	130
total carbohydrate (g)	12	12	13	13
protein (g)	8	8	8	8

Table S4. Nutritional content and sources of cheese used in this study.

type of cheese	string cheese	light string cheese
source/brand	Trader Joe's	Trader Joe's
serving size	28 g	28 g
calories	80	60
calories from fat	45	30
total fat (g)	5	2.5
saturated fat (g)	3	1.5
trans fat (g)	0	0
cholesterol (mg)	15	15
sodium (mg)	170	180
total carbohydrate (g)	>1 g	1
dietary fiber (g)	0	0
sugar (g)	0	0
protein (g)	8	6

Table S5. Nutritional content and sources of peanut butter used in this study.

label	Skippy Creamy Peanut Butter	Skippy Creamy Peanut Butter (reduced fat)
brand	Skippy's	Skippy's
serving size	2 tbsp (32 g)	2 tbsp (36 g)
calories	190	180
total fat (g)	16	12
saturated fat (g)	3	2
sodium (mg)	150	170
total carbohydrate (g)	7	15
sugar (g)	3	4
protein (g)	7	7

Table S6. Nutritional content and sources of oils used in this study.

label	toasted sesame oil	virgin pumpkin seed oil	virgin hempseed oil	pure olive oil	light olive oil	extra virgin olive oil	virgin avocado oil	safflower oil
brand	International Collection	International Collection	International Collection	Crisco	Crisco	Crisco	International Collection	International Collection
ingredients	toasted sesame oil	virgin pumpkin seed oil	virgin hempseed oil	refined olive oil, extra virgin olive oil	refined olive oil	extra virgin olive oil	virgin avocado oil	safflower oil
serving size	1 Tbsp (15 mL)	1 Tbsp (14g)	1 Tbsp (14g)	1 Tbsp (14g)	1 Tbsp (14g)	1 Tbsp (14g)	1 Tbsp (14g)	1 Tbsp (14g)
calories	130	130	130	120	120	120	130	130
calories from fat	130	130	130	120	120	120	130	130
total fat (g)	14	14	14	14	14	14	14	14
saturated fat (g)	2	2.5	1.5	2	2	2	2.5	1
trans fat (g)	0	0.5	0	0	0	0	0.5	0
polyunsaturated fat (g)	6	6	11	2	2	2	2	11
monosaturated fat (g)	6	5	1.5	10	10	10	9	2
cholesterol (mg)	0	0	0	0	0	0	0	0
total carbohydrate (g)	0	0	0	0	0	0	0	0
protein (g)	0	0	0	0	0	0	0	0

Table S6 continued. Nutritional content and sources of oils used in this study.

label	macademia nut oil	refined expeller pressed almond oil	refined expeller pressed walnut oil	canola oil	corn oil	sunflower oil	sesame oil	grapeseed oil
brand	International Collection	Whole Foods	Whole Foods	Shaw's	Shaw's	365 Everyday Value Organic	Whole Foods	International Collection
ingredients	virgin macademia nut oil	refined expeller pressed almond oil	refined expeller pressed walnut oil	canola oil	corn oil	organic expeller pressed refined high oleic sunflower oil	organic unrefined expeller pressed sesame oil	grapeseed oil
serving size	1 Tbsp (14g)	1 Tbsp (14g)	1 Tbsp (14g)	1 Tbsp (14g)	1 Tbsp (14g)	1 Tbsp (14g)	1 Tbsp (14g)	1 Tbps (15 mL)
calories	130	120	120	120	120	120	120	120
calories from fat	130	120	120	120	120	120	120	120
total fat (g)	14	14	14	14	14	14	14	14
saturated fat (g)	2	1	1.5	1	2	1	2	1
trans fat (g)	**0.5**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
polyunsaturated fat (g)	0.5	3	10	4	8	2	6	10
monosaturated fat (g)	11	10	2.5	9	4	11	6	3
cholesterol (mg)	0	0	0	0	0	0	0	0
total carbohydrate (g)	0	0	0	0	0	0	0	0
protein (g)	0	0	0	0	0	0	0	0

Table S7. Nutritional content and sources of grains used in this study.

type of grain	basmati rice (white)	basmati rice (brown)	short grain (white)	short grain (brown)	indian basmati (white)	indian basmati (brown)	long grain white	long grain brown
source/brand	Whole Foods	Whole Foods	Whole Foods	Whole Foods	Wild Harvest Organic	Wild Harvest Organic	Wild Harvest Organic	Wild Harvest Organic
serving size	1/4 cup uncooked (50 g)	1/4 cup uncooked (49 g)	1/4 cup uncooked (45 g)	1/4 cup uncooked (51 g)	1/4 cup uncooked (45 g)	1/4 cup uncooked (45 g)	1/4 cup uncooked (52 g)	1/4 cup uncooked (52 g)
calories	180	170	160	170	160	160	190	170
calories from fat	5	15	0	15	5	15	10	15
total fat (g)	0.5	2	0.5	1.5	0.5	1.5	1	2
saturated fat (g)	0	0	0	0	0	0	0	0
trans fat (g)	0	0	0	0	0	0	0	0
cholesterol (mg)	0	0	0	0	0	0	0	0
sodium (mg)	0	0	0	0	0	0	5	5
total carbohydrate (g)	41	38	36	40	35	35	41	39
dietary fiber (g)	0	2	1	3	1	2	0	2
sugar (g)	0	1	0	1	0	0	0	0
protein (g)	4	4	3	3	3	3	4	5

Table S7 continued. Nutritional content and sources of grains used in this study.

type of grain	forbidden rice (china black)	purple sticky rice	kamut	barley (pearled)	millet (hulled)	amaranth
source/brand	Whole Fods	Whole Fods	Whole Fods	Whole Fods	Whole Fods	Whole Fods
serving size	1/4 cup uncooked (48 g)	1/4 cup uncooked (50 g)	1/4 cup (48 g)	1/4 cut (50 g)	1/4 cup (47 g)	1/4 cut (49 g)
calories	160	185	140	180	150	180
calories from fat	10	1	10	5	10	30
total fat (g)	1.5	0	1	0.5	1.50	3
saturated fat (g)	0	0	0	0	0	1
trans fat (g)	0	0	0	0	0	0
cholesterol (mg)	0	0	0	0	0	0
sodium (mg)	0	4	0	0	0	10
total carbohydrate (g)	34	39	32	39	34	32
dietary fiber (g)	2	2	5	7	3	7
sugar (g)	<1	0	0	1	0	1
protein (g)	5	4	6	5	5	7

References:

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(2) Mirica, K. A.; Shevkoplyas, S. S.; Phillips, S. T.; Gupta, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **2009**, *131*, 10049-10058.

(3) Taylor, J. R. *An Introduction to Error Analysis*; University Science Books: Sausalito, CA, 1997.

(4) Sohnel, O.; Novotny, P. *Densities of Aqueous Solutions of Inorganic Substances*; Elsevier: New York, NY, 1985.