

that the expression for $\mu_{\text{kinetic}}^{\text{steady}}(V)$ can be extended to instantaneous sliding velocity. Velocity strengthening then leads to damping. It implies linear stability of steady sliding but does not prevent finite amplitude instability (stick-slip). Physically, damping may be related to vibrations induced by collisions between contact spots. Such a feature has been introduced in earthquake models to account for radiative elastic dissipation (see ref. 12 for example).

The low-speed regime of this study, together with standard results of rock-rock and metal-metal friction, provides strong support for the universality of low-velocity friction dynamics, which appears quite independent of the structure and nature of the underlying materials. Moreover, the criterion for the crossover to the high-speed regime being extremely simple, one may expect the inertial regime encountered in this study to also be of general relevance. Recent attempts to extend the range of validity of previous models¹¹ may include, as a phenomenological parameter, the crossover to the high-speed transition

reported here. A connection between this crossover and a microscopic length is provided here as an attempt to elucidate further the physical processes behind friction dynamics. □

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In situ speciation measurements of trace components in natural waters using thin-film gels

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RELIABLE measurement of trace species in natural waters is essential for studies of pollution or trace-element cycling, but is difficult, partly because the distribution of chemical species often changes during sampling and storage¹. *In situ* measurements can overcome these problems, but the few measurements made previously have involved complicated systems that cannot be used routinely^{1,2}. Here we describe a simple technique for measuring trace-metal concentrations *in situ* in water. The technique incorporates an ion-exchange resin separated from the solution by an ion-permeable gel membrane. Mass transport through the gel is diffusion-controlled and thus well defined, making it possible to obtain quantitative data on concentration and speciation over relatively short time periods (from one hour to several weeks). We present measurements of zinc concentrations in sea water using this technique which agree well with electrochemical measurements. In principle, our technique should be applicable to any inorganic or organic diffusing species.

In situ measurement of trace components in natural waters has proved an elusive goal. True equilibrium procedures, such as ion-selective electrodes or dialysis, suffer from poor sensitivity and selectivity or unrealistic equilibration times. Other speciation procedures, including anodic stripping voltammetry (in which metals are accumulated at an electrode before analysis) and the use of ion-exchange resins, are kinetically controlled and so the measured species depends on the chemical reaction involved and the rate of mass transport of ions from the bulk solution to the reaction site³. To provide quantitative measurements the mass transport must be controlled. Voltammetric measurements provide this control by relying on very short time measurements, externally induced convection or more recently on microelectrodes where diffusion processes dominate. Their capabilities for *in situ* measurements have been extensively

exploited for the measurement of oxygen, but reports of measurements of metals, which require relatively sophisticated on-site equipment³, are so far very limited¹. Ion-exchange resins and organic absorbants can be used for a wider range of components. But if they are simply suspended in bags in natural waters the rate of transport of ions from solution to the reaction site varies with time due to irregular convective processes, resulting in semi-quantitative data⁴. Here we introduce a new simple way of controlling mass transport which enables quantitative data on concentration and speciation to be obtained using any medium capable of reacting with the species of interest. The idea is simply to introduce a known thickness of gel between the solution and the reactive medium. Transport in the gel is restricted to diffusion and, by selection of an appropriate gel thickness, it controls the overall rate of mass transport irrespective of the hydrodynamics in the bulk solution. The procedure has provided *in situ* speciation measurements using simple, inexpensive and readily available equipment which are capable of theoretically sound interpretation.

Polyacrylamide gels have been used to provide measurements of pore waters by a new technique of diffusive equilibration in

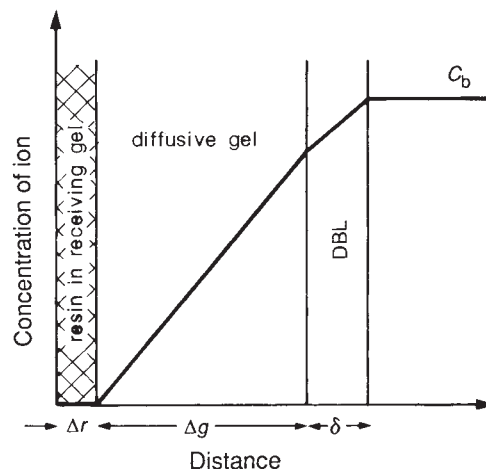


FIG. 1 Schematic representation of the free concentration of ionic species in a gel assembly in contact with natural water where the concentration is C_b (DBL, diffusive boundary layer.)

thin films (DET)⁵. Ions are simply allowed to diffuse into the gel until equilibrium with the pore waters is established. Here we have used a similar polyacrylamide gel, but have backed it by a further thin film (~150 µm thick) of gel containing a cation-exchange resin selective for trace metals (Chelex 100)⁶ close packed in a single layer of 75–150 µm spheres (Fig. 1). Within the layer of resin, of thickness Δr , the concentration of the free metal in solution is effectively zero, owing to the complexation by the resin which has been reacted to only a small fraction of its capacity. Within the bulk solution the metal has concentration C_b . The gel layer is assumed to be separated from the bulk solution by a diffusive boundary layer (DBL), of thickness δ , where transport is solely by molecular diffusion⁷. To be transported from the solution to the resin, ions must diffuse across the DBL and then through the gel, of thickness Δg . Small ions can diffuse freely through the effectively 2–5 nm pores⁸ of polyacrylamide gel with effective diffusion coefficients, D , indistinguishable from those in water⁹ (W.D. and H.Z., unpublished results). If for simplicity, it is assumed that $\delta \ll \Delta g$, Fick's laws can be used to define the flux of a given metal ion

$$\text{flux} = DC_b/\Delta g \quad (1)$$

The mass per unit area of resin, M_a , after time t is then:

$$M_a = DC_b t/\Delta g \quad (2)$$

and the concentration in the resin layer, C_r , is given by:

$$C_r = M_a/\Delta r \quad (3)$$

After a given time, the concentration in the resin layer, C_r , can be measured and the concentration in the solution can be quantified by:

$$C_b = C_r \Delta g \Delta r / Dt \quad (4)$$

Providing the resin is not saturated, the longer such a device is immersed, the more metal will be accumulated and the ratio of the concentration of metal in the resin layer to metal in solution will increase as the thickness of the resin and gel layers are decreased. Assuming a typical value of D of $10^{-5} \text{ cm}^2 \text{ s}^{-1}$, for a 24-h immersion, a gel layer thickness of 1 mm and a resin layer thickness of 0.1 mm, the concentration in the resin layer will be 864 times greater than the concentration in the bulk solution. Such a procedure therefore offers a large concentration enhancement for relatively short immersion times. This arrangement of a resin backing a gel relies on measuring a flux of metal over a given time. It depends on establishing a defined diffusion gradient in a thin film (DGT), in contrast to DET which depends on equilibrium being established. Equations (1)–(4) depend on the assumption that the thickness of the DBL between the gel and the bulk solution is negligibly small. The only available information on DBL thicknesses in natural waters applies to the sediment–water interface. In the bottom waters of stratified lakes or deep-sea locations, estimates of the DBL thickness are typically ~1 mm (ref. 7). Although definitive data are not available, various estimates suggest a range of 0.1–0.01 mm (ref. 10) may be appropriate in faster-moving waters, such as rivers and the surface waters of lakes and seas. If the gel layer is 1 mm thick, variation in δ between 0.1 and 0.01 mm could at most result in a change in flux to the Chelex of 10%. By ensuring that the gel layer is sufficiently thick, the DGT technique can in principle control the mass transfer of metal ions irrespective of changes in the velocity of water in the bulk solution.

The species measured by DGT can be appreciated by considering a simple equilibrium between free metal, M, and ligand, L. Binding between M and the resin effectively maintains M at a much lower concentration in the resin layer than in the bulk solution. If M binds more strongly to the resin than the ligand, L, and the release of M from ML is a fast process, there will effectively be a zero concentration of M and ML in the resin layer. Thus, as well as there being a concentration gradient for

M between the resin layer and the bulk solution (Fig. 1), there will be a concentration gradient for ML. If there is a very fast equilibrium between M and ML, they will both effectively contribute to the accumulating metal within the resin layer. For a very slow equilibrium only M will contribute. The physical gel layer between the resin and solution acts as a reaction layer which defines the measured species kinetically in an analogous fashion to an anodic stripping experiment, where the theory is already established¹¹. The thickness of the gel layer determines an effective time of measurement. At 1 mm thickness this characteristic time is ~5 min, longer than the 0.1–1.0 s typical of voltammetric experiments. DGT can therefore be expected to measure those species which (1) can readily dissociate in 5 min and (2) have a stability constant effectively smaller than that characterizing the binding of the metal to resin. The gel matrix can also be expected to exclude very large molecules. Although the above theory

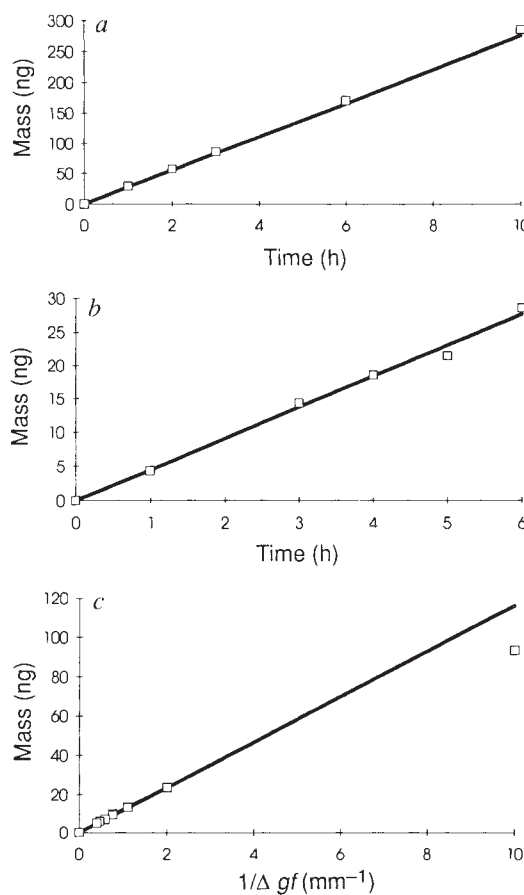


FIG. 2 a, Measured mass of zinc in the receiving resin (hollow squares) for gel assemblies suspended for different times in a stirred solution of natural sea water (pH 7.8) in the laboratory (28 °C). The concentration of labile zinc was measured by direct anodic stripping voltammetry to be 31 nM and was used with equation (2) to calculate the straight line. The good fit with the experimental data demonstrates the excellent agreement between anodic stripping voltammetry and the diffusion gradient in a thin film (DGT) technique in measuring labile zinc in a natural sea water sample. b, Measured mass of zinc in the receiving resin (hollow squares) for gel assemblies with a 0.4-mm gel layer suspended in sea water (Menai Straits, UK, salinity 32%, 14 °C) for various times. To prevent accumulation of particulates, the assemblies were covered with a 100-µm thick, 0.45-µm pore size Millipore cellulose nitrate membrane. Concentrations estimated without the membrane were indistinguishable. c, Measured mass of zinc in the receiving resin for gel assemblies of various combined gel and filter layer thickness, Δgf , exposed to sea water (as above) for 5 h 20 min. An inverse relationship is predicted by equation (2).

requires detailed validation, for example it may be compromised by metal fulvic complexes adsorbing directly to the resin, it is clear that this new speciation measurement is not dependent on the nature of the resin providing the reaction between free metal and resin is fast. Other sorbant or immobilized ligands, which could compete effectively with the solution ligands and would not adsorb metal complexes, could be used and the same species would be measured.

To test these principles, gel assemblies were constructed using a 10.5 cm diameter, 1.3 cm total thickness perspex disc containing layers of gel and resin (Fig. 1). The gel was exposed through a 5.0 cm diameter window; a set of screws and an 'o'-ring prevented ingress of water to the side or back of the gel while holding the layers of gel firmly onto the perspex backing. After casting, polyacrylamide gel was hydrated in water for at least 24 h to ensure dimensional stability before use. The resin was embedded in a separate ~ 150 μm -thick gel as a single plane of approximately close-packed beads. After immersion, the gel layer was peeled off, metal extracted from the resin layer with 1 ml of 2 M HNO_3 and measured using atomic absorption spectroscopy. Self-diffusion coefficients for Zn for the appropriate temperatures⁹ were used. Gel thicknesses should be entirely reproducible as they are determined by casting. The thickness of the hydrated gel was measured by a travelling microscope and was accurate to better than 4%.

Laboratory exposures of gel assemblies to stirred solutions of $\sim 10^{-7}$ M $\text{Zn}(\text{NO}_3)_2$, with and without added NaCl (0.5 M), showed that the concentration of metal measured in the resin layer could be predicted quantitatively (97–100%) by equation (4). Measurements of Zn in pH-adjusted sea-water, covering the pH range 4.8–7.8, by direct anodic stripping voltammetry without sample pretreatment and by gels exposed to stirred solutions were in good agreement (Fig. 2a). In an unstirred solution recovery was only 60%, indicating that mass transport was partly limited by the DBL in solution. On lowering the pH to 2.5, recovery was greatly reduced, consistent with the properties of Chelex 100.

In natural sea water, particles adhere to the gel surface and so may affect the inward diffusion of metal ions. Covering the gel with a 100 μm -thick, 0.45- μm pore size cellulose nitrate membrane prevented the particles sticking. Diffusion through the filter was indistinguishable from that through a similar thickness gel. Varying the time of *in situ* immersion in sea water (Fig. 2b) resulted in mass increasing linearly with time. As the tidal current varied from 0 to ~ 4 knots during this time, the thickness of the DBL will also vary. Consequently the linear response indicates that the gel thickness is dominating the control of mass transport confirming the assumption that the DBL is negligible. The mean concentration from these measurements was very reproducible at 11.9 ± 0.4 nM as compared to 26.5 ± 2.8 nM from seven samples taken at hourly intervals and measured by anodic stripping voltammetry after acidification to pH 2 and exposure to ultraviolet irradiation. A difference is to be expected if it is considered that DGT only measures labile species and therefore will exclude kinetically inert organic species and large colloids.

To investigate further the effect of the gel layer, assemblies of different gel thicknesses, covered by 100 μm -thick filters, were exposed to sea water for 320 min. Consistent with equation (2), the mass measured in the resin was inversely proportional to the total thickness of the filter and gel layer (Fig. 2c), except for when there was no gel layer and only a 100- μm filter was used. The reduced recovery for the 100- μm case can be used to provide an estimate of the mean effective thickness of the DBL of 30 μm .

These measurements demonstrate that the theoretical principles of the DGT technique hold for practical *in situ* use. By using a gel to define the diffusion layer thickness, the mass transport of the system and the criteria for defining the measured species are effectively defined. Using a 0.5-mm diffusion layer, as in these experiments, a concentration factor of 72 is obtained by a 1 h immersion. Such a procedure using simple equipment

immediately overcomes most contamination problems that beset trace metal measurements. The technique is suitable for deployment from aboard ship and a time of 1 h is appropriate for sensing temporal changes in trace metal concentrations in sea water. Changes during tidal cycles could potentially be measured, especially as the technique is independent of ionic strength and pH. Moreover, as the capacity of the resin should allow 3 months immersion in relatively contaminated coastal waters before saturation is reached, the device can readily be used to provide a long-term (weeks, months) integrated record of trace metal concentrations. The limiting factor will most likely be the effects of biofouling, but there is certainly potential for the use of DGT as a chemical alternative to shellfish for providing integrated records of trace metal pollution¹². DGT is in principle applicable to most trace metals in any non-acid aqueous medium, although the detailed use in complicated solutions like fresh waters, where colloidal material is very important, requires further testing. This new measurement principle can theoretically be applied to any component, including organics, that can readily diffuse through a gel layer and be consumed by an active component in a backing layer. □

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Western boundary currents in the atmosphere of Mars

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WESTERN boundary currents (WBCs) are an intensification of north–south flow adjacent to an eastward-facing meridional boundary. Although most familiar in the oceans (where the Gulf Stream is the best known example), WBCs also occur in the Earth's troposphere, the main example being the East African Jet¹, which is thought to play an important role in the Asiatic monsoon. Here we identify boundary currents in a different geophysical context: a numerical simulation of the atmosphere of Mars. In our simulation, WBCs exist in association with significant cross-equatorial flow and the presence of equatorial martian topography, which has vertical scale far exceeding terrestrial relief². The intensity and width of these currents depend on model parameters, notably the surface drag. From a comparison of our results with other martian models we suggest that WBCs have already been simulated, although they were not previously identified as such³. The available observational evidence appears to be consistent with the presence of martian WBCs, which may be important in the generation of global and great dust storms.