



Real-time vapour sensing using an OFET-based electronic nose and genetic programming

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ABSTRACT

Electronic noses (e-noses) are increasingly being used as vapour sensors in a range of application areas. E-noses made up of arrays of organic field-effect transistors (OFETs) are particularly valuable due the range and diversity of the information which they provide concerning analyte binding. This study demonstrates that arrays of OFETs, when combined with a data analysis technique using Genetic Programming (GP), can selectively detect airborne analytes in real time. The use of multiple parameters – on resistance, off current and mobility – collected from multiple transistors coated with different semiconducting polymers gives dramatic improvements in the sensitivity (true positive rate), specificity (true negative rate) and speed of sensing. Computer-controlled data collection allows the identification of analytes in real-time, with a time-lag between exposure and detection of the order of 4 s.

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1. Introduction

The detection of gases has a wide range of applications in a number of fields including air-quality monitoring [1], food spoilage detection [2], environmental protection [3], homeland security [4] and medical diagnostics [5]. Currently, sensors use a variety of detection methods including spectrometry of various types [6–9], surface plasmon resonance [10], catalytic bead sensing [11] and carbon nanotube sensing [12]. Early sensors used a single measurement to identify a particular chemical, or family of chemicals. More recently, electronic noses, or ‘e-noses’, have been developed [13,14], using a variety of technologies including chemiresistors using metal oxides [15] or conducting polymers [16], optical sensors [17] and mass sensors [18]. Like biological noses, these contain arrays of sensors, resulting in multiple measurements which are then analysed using pattern recognition techniques. Theoretically, this multiparametric approach confers the ability to identify a very large number of different chemicals with high specificity. Indeed, with a sufficient number of carefully chosen sensing elements, an e-nose could be a near-

universal vapour sensor. In practice, however, all existing e-noses detect only a family of related chemicals, primarily due to the difficulty of producing the variety of sensing materials required for universal sensing [19]. The great majority of existing sensors are further limited by the requirement for measurements taken after a sensor has reached an equilibrium state [13], resulting in typical response times of 5–10 min [14]. For safety-critical tasks, such as the detection of poisonous vapours, this time-lag is clearly problematic.

Sensors based on organic semiconductors are highly suitable for vapour detection applications, owing to their ability to rapidly absorb analytes at room temperature, frequently affecting a number of their measurable electrical properties. Organic field-effect transistors (OFETs) are transistors which contain 3 terminals, known as source, drain and gate and which use organic semiconducting polymers in their conductive channel. They have recently been developed as low-cost electronic products for use in flexible devices [20], light-emitting displays [21], pressure sensors [22] and chemical sensors [23].

OFETs generally have low detection limits and, if carefully designed, can also have low threshold voltages, short response and recovery times, high signal-to-noise ratios and good selectivity [24]. An important, but largely unexploited, advantage of transistors is that a number of different parameters may be extracted from

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each one [25], enriching the data available during vapour identification. When used within an e-nose, as here, OFETs have a further vital advantage. A very large number of different active materials may be created by the polymerisation of different monomers, so affecting the interaction between analyte and transistor. Observed substituent effects include polarisation [26], steric hindrance [27] and acid–base interactions [23]. The wide variation in OFET response offers the possibility of an array of transistors, each of which can add information for use during pattern recognition [26].

Here, we describe a method that *combines* the use of multiple OFETs with the collection of multiparametric data from each OFET, so that a large number of predictive features may be extracted from a modestly sized sensor array. The high dimensionality of the resulting data necessitates the use of a pattern recognition technique and we demonstrate the use of genetic programming (GP) for this task.

The main drawbacks of OFETs have been the overheads required, both in terms of data collection and analysis and in the hardware required to support them. However, recent advances in both the hardware and software associated with single OFET sensors have resulted in a substantial increase in the portability of such instruments and the speed and reliability with which detection may be performed, as we have reported previously [23]. This paper builds on these technological advances, by showing that they can be extended to *arrays* of sensors. The practical utility of these techniques is shown through the detection of dimethyl

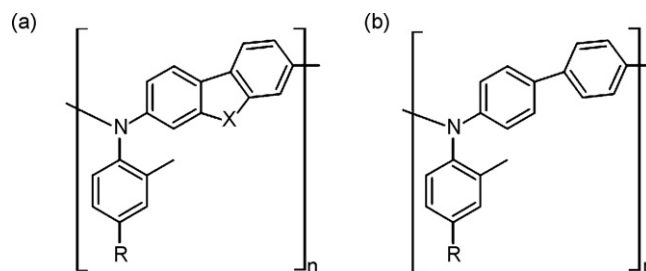


Fig. 1. Structure of the polymers used as sensing materials: (a) polymer 1 ($X = \text{CH}_2$, $R = \text{OMe}$), polymer 3 ($X = \text{S}$, $R = \text{Me}$); (b) polymer 2 ($R = \text{OMe}$), polymer 4 ($R = \text{Me}$).

methylphosphonate (DMMP), a precursor to organophosphate nerve agents, as well as acetone, methanol and propan-1-ol.

2. Experimental

2.1. Polymer structures and preparation

Here, we use 4 OFETs based upon polytriarylamines (PTAAs) as shown in Fig. 1. These semiconducting polymers [28] have electrical properties that respond reversibly to low-level exposure to nitrogen dioxide, alcohols and other vapours [23,29]. An important reason for using PTAAs is that they are amorphous. While

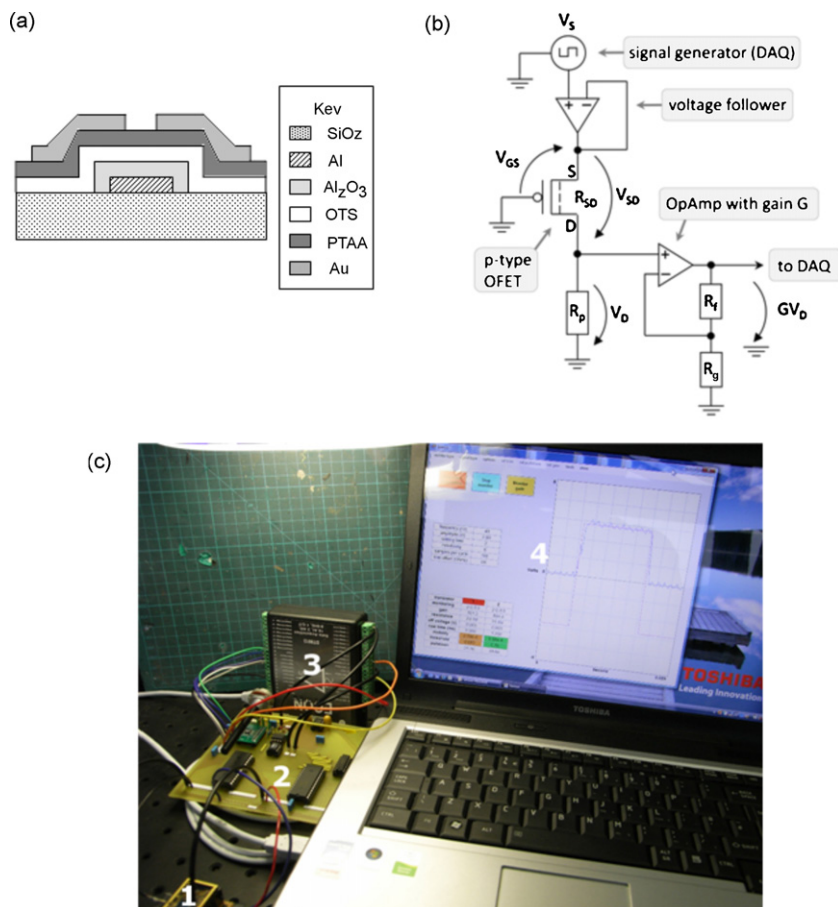


Fig. 2. Equipment used during data collection. (a) Cross-section of an OFET used in this study. An aluminium ‘finger’ represents the gate terminal and the gold contacts are the source and drain terminals. Polytriarylamine (PTAA) is the polymer used as a sensing layer and octadecyltrichlorosilane (OTS) improves the device performance by moderating the surface polarity. (b) Diagram of the circuit used to characterise the OFETs. The operational amplifier (‘OpAmp’), together with the fixed resistor R_f and variable gain resistor, R_g , acts as a voltage amplifier with gain. The gain, G , is defined as $G = R_g/R_f + 1$. V_s , R_g and R_p all are controlled by the data acquisition device (DAQ), which also measures the circuit output voltage, which has the value GV_D . (c) Photograph of our experimental set-up showing (1) OFET in a standard socket (to be placed in exposure chamber), (2) the electronic circuit illustrated in Fig. 1b, (3) the data acquisition device (DAQ) and (4) the laptop displaying the user interface of the controlling program.

semi-crystalline polymers give higher mobilities they may be less effective as sensing materials since the presence of grain boundaries leads to greater variation between devices [30]. The particular polymers shown in Fig. 1 were chosen to provide materials with varying electron-donating properties and flexibilities.

Polymers 1–3 were prepared by modification of a microwave-assisted method reported previously [31]. The requisite aniline and dibromoaryl (1 equiv.) were dissolved in degassed toluene. Sodium-*t*-butoxide (3.2 equiv.), tris(dibenzylideneacetone) dipalladium(0) (1 mol%) and tri-*t*-butylphosphine (6 mol%) were added and the mixture stirred under nitrogen in an oil bath at 100 °C for 10–30 min. The polymerisations were quenched by the addition of 4-bromoanisole which acts as an end cap. The products were rigorously purified and obtained as bright yellow solids. Polymer 4 was obtained commercially as a blend with poly(α -methylstyrene) from Merck.

2.2. Transistor preparation and structure

The transistor preparation procedure has been described in detail previously [32]. The transistors were initially prepared by evaporating aluminium under a 10^{-6} Torr vacuum onto UV-ozone cleaned 100 nm Si/SiO₂ wafers and anodising the sample to 5 V to produce ~8 nm thick Al₂O₃ dielectric layer, which acted as a high-capacitance gate insulator in the bottom-gate. The substrates were then treated using octadecyltrichlorosilane (OTS). The insulating layer had a capacitance of 640 nF cm⁻². The devices were then spin-coated with solutions of the semiconducting polymers in toluene and rectangular gold top contacts (2 mm × 1 mm) were added using evaporation through a shadow mask. The channel widths and lengths were 2 mm and 10 μ m, respectively, with a maximum error of 0.5 μ m. The OFET structure used in this study is illustrated in Fig. 2a.

2.3. Electronic components

For p-type semiconductors, as used here, a conductive accumulation layer is established in the transistor channel on the application of a sufficiently large negative voltage to the gate terminal. The minimum gate voltage required to establish an accumulation layer is called the 'threshold voltage', V_T . V_T is a convoluted function of the properties of all components of the OFET, and is one of the device's most important characteristics. Above V_T , the OFET is said to be 'on'; below V_T it is said to be 'off'. The existence, and conductivity, of the accumulation layer is probed by the application of a voltage to the drain terminal, and measurement of the resulting drain current, I_D .

In our method, transistors are characterised using the circuit shown in Fig. 2b, using the 'gain method' [32]. The gate terminal is grounded, and the drain terminal is linked to ground by a small resistor, R_p , so it is effectively grounded, too. A square wave of amplitude $\pm V_S$ is applied to the source terminal by a data acquisition device (DAQ), to switch the OFET 'on' and 'off' periodically. The DAQ also adjusts R_p and trims gain, G , so that $GV_{D(on)} = V_S$. R_p is selected to have a value of approximately $R_{SD}/1000$, so V_D is negligible. Under these conditions the 'on' resistance, R_{SD} , and 'off' current, $I_{D(off)}$ may be calculated using the relationships $R_{SD} = GR_p$, and $I_{D(off)} = GV_{D(off)}/R_{SD}$. $I_{D(off)}$ is an important parameter since it indicates the bulk conductivity of the polymer, whereas R_{SD} is an indication of its conductivity in the presence of a field-effect.

The circuit shown in Fig. 2b has been implemented on a bespoke printed circuit board (PCB). R_p is the programmable resistor AD7376 from Analog Devices, which can have its resistance set to one of 128 values, up to 1 M Ω , using a 7-bit data-word. Gain, G , is applied via a voltage divider using a fixed resistor, R_f , of resistance 2 M Ω and a variable 'gain resistor', R_g , which is the pro-

grammable resistor AD5235 from Analog Devices. This has 1024 possible resistances up to 25 k Ω (corresponding to $G \approx 80$), set via a 10-bit data-word.

2.4. Data collection and pre-processing

Data collection may be performed at a fixed V_S or using a series of stepped V_S values. The advantage of the second procedure is that additional parameters – threshold voltage V_T and mobility, μ – may be calculated from a series of $I_{D(on)}$ values, obtained at different V_S . These quantities are important electrical properties of the OFET, and contain valuable discriminatory information in sensor applications [25]. $I_{D(on)}$ is typically in the nanoamp region for the OFETs used in this study, and its measurement traditionally involves the use of expensive, manually operated equipment and is therefore impractical for use in a portable vapour sensor. However, use of the circuit in Fig. 2b circumvents this difficulty. The described electrical drive scheme ensures that the OFET always operates in the 'saturation' regime, when it is 'on', i.e. above V_T . In this regime, Eq. (1) holds [32], where W and L are the width and length of the transistor channel and C_i is the gate oxide capacitance per unit area. It follows that a graph of $(V_S/G)^{1/2}$ against V_S will render a straight line with an x -intercept equal to V_T and a slope proportional to $\mu^{1/2}$. Rather than physically drawing a graph, a line of best fit may be calculated *in silico* via least-squares optimisation and hence μ and V_T inferred.

$$\frac{V_S}{G} = \frac{W}{2L} R_p \mu C_i (V_S - V_T)^2 \quad (1)$$

The method just described has been applied previously to a single transistor [23,32]. The sensing equipment reported here extends this method into an electronic nose, through the use of 4 transistors, each coated with a different polymer.

The time taken for quick (fixed-voltage) characterisation is approximately 0.7 s. During full (stepped voltage) characterisation we use 6 different voltages, so the time required for full characterisation of each transistor is approximately 4 s. In our experiments a simple digital switch allows the characterisation of one transistor at a time, so the time for full characterisation of all 4 transistors is of the order of 15 s and for quick characterisation is approximately 3 s. The times required would scale up linearly with more transistors. However, in principle a commercial implementation could characterise all transistors in parallel, thereby reducing the full characterisation time to 4 s and the quick characterisation time to 0.7 s, for any number of transistors.

Previous sensor arrays have usually been allowed to reach an equilibrium state before measurements are made [13], for 2 reasons. The first is that manual characterisation of transistors is a fairly slow process. In particular, the calculation of μ and V_T requires measurements at several voltages and these have had to be made under steady-state conditions to avoid temporal changes in G affecting the validity of Eq. (1). The speed of our automated characterisation method largely solves this problem: except in the presence of very fast gain changes, obtaining measurements every 0.7 s is sufficiently fast to achieve a pseudo-steady-state condition, in which changes in G between measurements may be neglected during the calculation of μ and V_T , even though a true steady-state (chemical equilibrium) has not been reached. The second reason is that pattern recognition methods have been insufficiently flexible to accurately classify time-varying data [33]. To solve this problem, we have used genetic programming (GP) to perform pattern recognition, as described in Section 1.8.

For each transistor and each analyte, data were collected for 6 min: 2 min pre-exposure; 2 min exposed; and 2 min recovery. This corresponds to approximately 90 measurements for each transistor. The present study uses the exposed data plus 5 baseline

data, sampled immediately before exposure, resulting in approximately 35 points for each transistor. To ensure that the transistors were 'on', V_S amplitudes were set well above V_T values. For polymers 1–4 the respective unexposed V_T values were 0.15 V, -0.3 V, -0.7 V, -1.5 V and the V_S ranges were 1.2–2.2 V, 1.5–2.5 V, 1.5–2.5 V and 2.2–3.2 V. During fixed-voltage characterisation, V_S was taken from the middle of the V_S range.

In full characterisation mode, 4 properties (average R_{SD} , average $I_{D(off)}$, μ and V_T) may be deduced for each of 4 different transistors. However, the V_T values were found to be highly variable because the extrapolation procedure is very sensitive to noise. V_T was not therefore used for pattern recognition, leaving 12 properties. In quick characterisation mode, μ values are unavailable, so there are just 8 available properties. We used the values of these properties as inputs to a GP. Immediately before exposure, 5 consecutive measurements were taken and these values were averaged to give a baseline measure. The inputs to GP were then the differences between the measured values and this baseline, starting immediately after exposure.

Before being used in GP, all data were normalised to a range of $[-1, +1]$ using a linear transformation. This prevents individual parameters from dominating the pattern recognition task as a result of a large range, rather than their inherent predictive value.

2.5. Data acquisition

The acquisition of data for transistor characterisation was fully controlled by a bespoke program running on a laptop computer. This program has been written in the Visual Basic language, using the DT-Open Layers and DT-Display class libraries provided with the data acquisition module DT9813 from Data Translation Inc. R_p and R_g are optimised via a series of estimates, based upon the knowledge that the measured output voltage is proportional to R_p and G . R_p is set once (before exposure) by setting the gain to 1000, V_S to the midpoint of the range of voltages to be applied and then adjusting R_p until the output on-voltage is equal to V_S . This ensures that the measured gain values will be in the region of 1000, which we have found empirically to give highly stable measurements. R_p is then fixed and the tasks of setting the amplitude of V_S and adjusting the gain are alternated.

The interface between the laptop controller and the PCB was provided by the DT9813 module. A USB connection services all of the digital inputs and outputs to this module as well as providing power. The DT9813 has the following input/output (IO) channels:

- 2 analogue output channels. One is used to supply voltage to power one of the components on the PCB. The other provides the oscillating V_S signal, at a frequency of 30 Hz.
- 16 analogue input channels. In the set-up reported here, only 2 analogue input channels are used: one for the output of the PCB, i.e. GV_d , and one for the supply voltage V_S . The additional channels will be used in the future when (and if) transistors are characterised in parallel rather than in series.
- 4 digital output channels. These are used to control (program) components on the PCB.
- 4 digital input channels. One of these is used to monitor the counter component on the PCB, so that it can be re-set upon reaching its final (16th) position.
- Fixed 0 V (ground), +2.5 V and +5 V analogue outputs, which provide power to some of the PCB components and provide the gate voltage (equal to 0 V) to the transistors.

Fig. 2c is a photograph of the experimental set-up, showing an OFET, the PCB, the DAQ and a laptop running the controlling program.

2.6. Transistor exposure

The data used for pattern recognition was collected separately for each transistor, due to technical difficulties in accommodating 4 transistors in the exposure chamber and in order to obtain more frequent measurements from each transistor. However, the laptop program is capable of collecting data from up to 16 transistors near-simultaneously, by cycling through the transistors. In future we intend to expose 4 (or more) transistors simultaneously.

OFETs were connected by copper wires to the source, drain, and gate contacts with Leit-C glue (Fluka) [29]. They were separately exposed to 4 different vapours containing, respectively, acetone, DMMP, methanol and propan-1-ol (Sigma-Aldrich). The vapours were prepared by bubbling nitrogen through the liquids at a controlled flow rate of 25 standard cubic centimetres per minute (sccm) and a constant temperature of 22 °C. The resulting vapour concentrations were 480,000, 2500, 270,000 and 35,000 ppm, respectively. Prior to delivery through a Teflon tube close to the transistor channel, the concentrations of the generated vapours were halved by mixing with 25 sccm of pure nitrogen [23]. The resulting concentrations are higher than those required by commercial sensing devices and further investigation is required to test the lower detection limit of the device, i.e. the point at which the signal-to-noise ratio makes detection impossible. The flow rates of the vapours and of nitrogen were controlled by a Tylan FC-260 mass flow controller. The volume of the exposure chamber was approximately 900 cm³. However, the delivery tube was directed straight at the transistor at close proximity, in order to minimise the time required to displace the gas in the vicinity of the transistor.

2.7. Classification task

All of the transistors showed a large response upon exposure (partly as a result of the relatively high concentrations used in this demonstration), so separating the data for the exposed and unexposed states is a trivial task. Here we present the results of performing a more difficult task, that of distinguishing between the responses to the different vapours. Separate GPs were evolved to identify each vapour, i.e. to classify the collected data into is/is not acetone, is/is not DMMP, is/is not methanol and is/is not propanol.

2.8. Genetic programming (GP)

GP is a highly flexible method for solving a variety of problems, inspired by the process of Darwinian evolution via selection, reproduction and mutation [34]. It randomly generates a 'population' of possible solutions to a problem. In this case, the solutions are mathematical functions that relate the input variables to a prediction of the presence/absence of a particular analyte. Each solution is represented as a tree: a possible solution is illustrated in Fig. 3. Each solution has an associated 'fitness'. In this case, the fitness measure is the area under the receiver-operator characteristic (AUROC). This is a measure of the extent to which a function can separate positive and negative cases, commonly used as an indicator of the effectiveness of medical diagnosis [35]. An AUROC value of 1.0 indicates that positive and negative cases are completely separable, i.e. a cut-off value may be chosen such that all positive cases give an output above this value and all negative cases give outputs below this value. On the other hand an AUROC value of 0.5 indicates that a predictor gives results that are no better than random. Intermediate AUROC values may be compared to show the relative efficacy of different predictors.

The population of candidate solutions undergoes a process of simulated 'evolution'. Those solutions that have a relatively high AUROC are selected for 'reproduction'. Either a single parent is randomly mutated to produce offspring or 2 parents are selected for

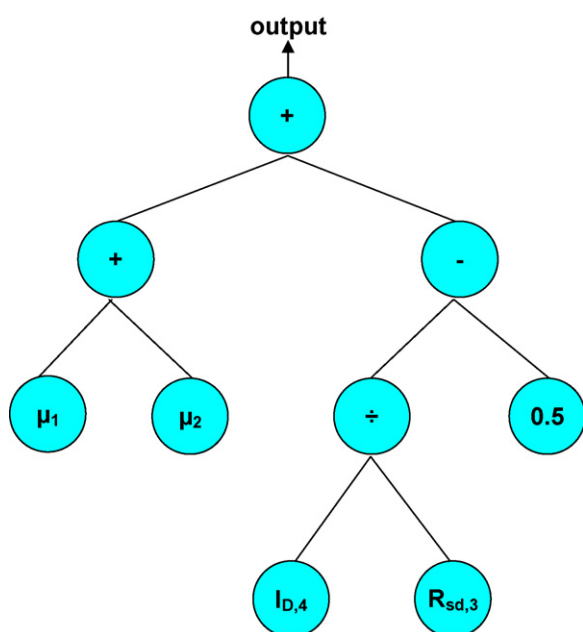


Fig. 3. A possible GP solution. It represents the function, $output = \mu_1 + \mu_2 + I_{D,4}/R_{sd,3} - 0.5$. Most GP solutions are much more complex, containing over 50 nodes, on average. All inputs (R_{SD} , I_D and μ values) are normalised to a range of $[-1, +1]$ in a pre-processing step before use in a GP, to prevent variables with a large range from dominating the functions produced.

re-combination. During the former, a subtree is randomly removed from the parent and replaced by a new randomly generated subtree. In the latter operation, a cut-point is randomly selected in each parent and the subtrees below these cut-points are swapped between the parents to produce 2 new offspring. Initially, the average fitness of the population is poor. However, as a result of the repeated production of offspring and the replacement of less fit parents by these new solutions, the average fitness of the population increases. After several generations have passed, the average fitness no longer improves. At this point, the best solution is identified as the output of the GP.

A population of 100 solutions was used. The starting population was generated randomly using the 'ramped half-and-half' [34] method, which gives candidate solution-trees with a variety of shapes and sizes. Terminals were randomly chosen from the set of all inputs together with a set of constants of the same size as the input set and a range of $[-1.0, 1.0]$. For example, if there were 6 inputs being used, the constant set would be made up of the set $\{-1.0, -0.6, -0.2, 0.2, 0.6, 1.0\}$. Non-leaf nodes were randomly selected from the function set $\{+, -, \times, \div, \text{IF, NOT, AND, OR, MIN, MAX}\}$. Evolution was carried out in steady-state mode, whereby individual solutions were replaced one at a time, using 'tournament selection'. In this procedure, the parent(s) of the new solution were selected as the best of 4 randomly selected solutions. Similarly,

Table 1

Combinations of transistors used in training GPs. 100 runs were performed using each of the 15 different combinations shown.

No. of transistors	Polymer 1	Polymer 2	Polymer 3	Polymer 4
1	✓	✓	✓	✓
2	✓ ✓ ✓	✓ ✓ ✓	✓ ✓ ✓	✓ ✓ ✓
3	✓ ✓ ✓	✓ ✓ ✓	✓ ✓ ✓	✓ ✓ ✓
4	✓	✓	✓	✓

the solution to be replaced was selected as the worst individual in a randomly selected 4-way tournament. The occurrence of 100 replacements was considered to constitute a 'generation'.

The data were divided using stratified sampling into training, validation and test sets in the ratio 6:3:1. GPs were evolved using the training set to obtain AUROC values. Evolution was stopped once there had been no improvement in the average AUROC value on the validation set for 25 generations. The best solution was then selected, based on AUROC values, and a cut-off value was set so as to minimise the quantity $(FPR^2 + FNR^2)$, where FPR is the false positive rate and FNR is the false negative rate, upon applying the chosen function to a combined data set containing the training and validation data. The chosen function and cut-off were applied to the test set in order to obtain sensitivity and specificity values.

Assuming that data from between 1 and 4 different transistors are used in GP training results in 15 possible combinations of transistors, as listed in Table 1. For each combination, 100 runs were performed, with data partitioned such that every point appeared in a test set 10 times, in order to assess the reliability of the GP predictions.

3. Results

3.1. Area under the receiver-operator characteristic (AUROC)

AUROC values for all possible combinations of 1, 2, 3 or 4 transistors are given in Table 2, with standard deviations across 100 runs in brackets. The AUROC values are graphed in Fig. 4. They show that increasing the amount of data available by the addition of extra transistors leads to an increase in AUROC values. The standard deviations indicate that the reliability of the results is also improved.

Table 2

Average AUROC values for GP predictions (with standard deviations in brackets). Values are obtained for predictions on test data. They have been averaged across all possible combinations of transistors, repeated 100 times with different partitions of training and test data.

Characterisation mode	Number of transistors	Acetone	DMMP	Methanol	Propanol	Average
Quick	1	0.77(±0.15)	0.74(±0.16)	0.74(±0.16)	0.69(±0.17)	0.73(±0.16)
	2	0.85(±0.12)	0.82(±0.14)	0.82(±0.14)	0.75(±0.17)	0.81(±0.14)
	3	0.92(±0.09)	0.86(±0.14)	0.84(±0.14)	0.77(±0.16)	0.85(±0.13)
	4	0.98(±0.09)	0.87(±0.15)	0.89(±0.16)	0.77(±0.16)	0.88(±0.14)
Full	1	0.81(±0.13)	0.77(±0.14)	0.84(±0.14)	0.76(±0.15)	0.79(±0.14)
	2	0.88(±0.11)	0.88(±0.12)	0.88(±0.13)	0.82(±0.14)	0.86(±0.12)
	3	0.93(±0.09)	0.92(±0.09)	0.91(±0.11)	0.86(±0.13)	0.91(±0.10)
	4	0.98(±0.07)	0.94(±0.09)	0.91(±0.11)	0.87(±0.13)	0.92(±0.10)

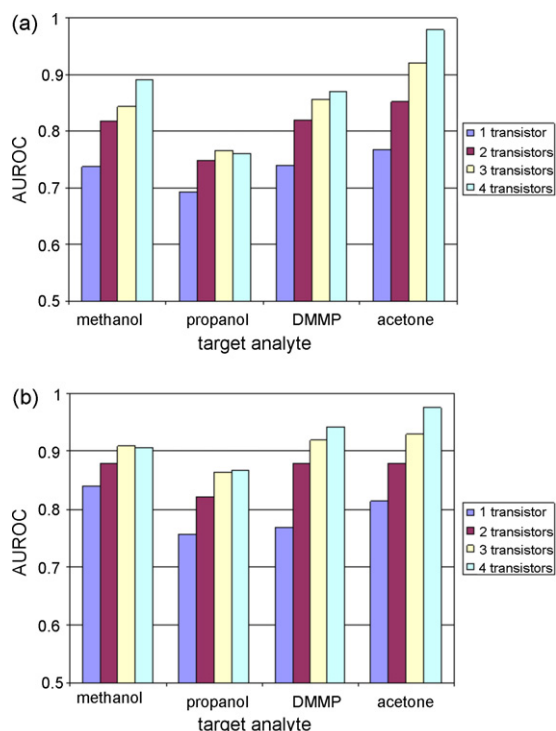


Fig. 4. Area under the receiver-operator characteristic (AUROC) values for GP predictions. Values are obtained for predictions on test data. They have been averaged across all possible combinations of transistors, repeated 100 times with different partitions of training and test data. A value of 1.0 indicates complete discrimination between the presence and absence of an analyte while a value of 0.5 indicates a null (random) prediction. (a) The results using a quick (fixed-voltage) regime; (b) the results for a full (stepped-voltage) regime.

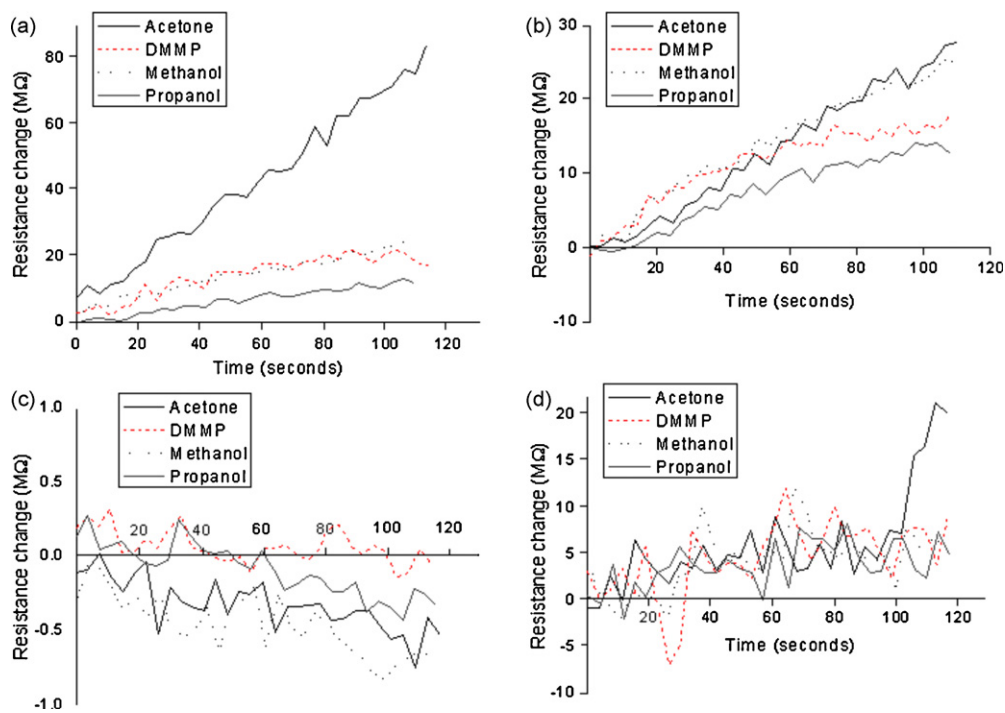


Fig. 5. Graphs of the change in R_{SD} ($M\Omega$) with exposure time (seconds) upon exposure to 4 different analytes, for OFETs coated with 4 different polymers. The subfigures refer to data collected from, respectively, (a) polymer 1, (b) polymer 2, (c) polymer 3 and (d) polymer 4. The graphs illustrate the difficulty of separating analyte responses using a univariate approach.

A comparison between ‘quick’ and ‘full’ modes of data collection (Fig. 4a and b) indicates that the latter is, unsurprisingly, more informative. However, it should be noted that the use of 4 transistors in ‘quick’ mode gives AUROC values that are as good as those values obtained from 1 transistor characterised in ‘full’ mode, despite taking two-thirds of the time to collect data. This comparison suggests that a 2-phase detection method – involving initial screening at a fixed-voltage followed by full characterisation if the target gas is indicated by the first phase – might be an effective compromise between speed and reliability.

Using data from 4 transistors in full characterisation mode leads to the highest observed AUROC values. Predictors were created for this data by selecting cut-off values above which a vapour was predicted to be present, as described in Section 1.8. The resulting classifiers had average sensitivity (true positive rate) and specificity values of 0.91 and 0.96 for acetone, 0.86 and 0.88 for DMMP, 0.79 and 0.87 for methanol, and 0.79 and 0.83 for propanol.

3.2. Input use analysis

In addition to yielding highly specific detection, GPs automatically select the most valuable inputs to use during prediction. Each predictor uses a different mathematical function and an analysis of the functions used yields the frequency with which a parameter from a particular polymer or a particular data-type (R_{SD} , $I_{D(off)}$ or μ) was used in the solutions. Table 3 indicates that, while all predictors are multiparametric, some emphasise the role of particular parameters in carrying out a particular classification. For example, GPs that predict the presence of acetone tend to use R_{SD} values while predictors of propanol are more likely to use a mixture of different parameter types. However, the preference for specific parameters is not highly pronounced for the detection of any analyte, confirming the usefulness of a multiparametric, multisensor approach.

Table 3

Average usage of data from each polymer and parameter-type. Values represent the number of times each type of input was used by the GPs, averaged across 100 GP runs in which all 12 parameters were used.

Analyte	Polymer				Parameter-type		
	1	2	3	4	R_{SD}	$I_{D(off)}$	μ
Acetone	6.9303	4.1177	2.2864	1.835	9.5347	3.4364	2.1983
DMMP	2.5357	4.6987	7.0503	2.1033	9.4203	3.5646	3.4031
Methanol	7.5966	2.6388	4.2191	3.686	7.7188	5.5472	4.8745
Propanol	5.319	4.699	1.6997	3.8184	6.4998	3.7987	5.2376

3.3. Univariate analysis

Univariate analysis gives further confirmation of the need for a multiparametric approach. A comparison between the data collected during exposure to the different analytes shows that there is very strong overlap in the ranges of any individual variable. This is illustrated by Fig. 5, which shows the changes in R_{SD} for all 4 OFETs exposed to all 4 analytes. For any one polymer, the range of changes in R_{SD} is similar for most or all of the tested analytes. For this reason, it is not possible to separate the responses to different analytes using univariate analysis. However, multivariate analysis, as used by GP, results in very good separability, as shown in Section 2.1.

4. Conclusion

In conclusion, OFET arrays have been shown to be effective vapour sensors, with high sensitivity (true positive rate) and specificity (true negative rate). The effectiveness of these arrays has been shown to arise both from the use of multiple OFETs and from the acquisition of multiple parameters from each OFET. The use of an automated gain method of characterisation, combined with the use of GP-based pattern recognition techniques, allows real-time monitoring of gaseous environments, with response times between initial exposure and detection of a few seconds. Future work will focus on the development and testing of polymers with increased specificity for specific analytes and with clear responses at low analyte concentrations. The use of larger arrays, containing alternative organic semiconductors, is expected to further increase the scope and reliability of this type of e-nose, with the ultimate goal of creating a universal vapour sensor.

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